



INFLUENCE OF SOURCE ROCKS ON GEOCHEMISTRY OF SEDIMENTS OF THE KING GEORGE ISLAND, ANTARCTICA: EVIDENCE FROM TRACE AND RARE EARTH ELEMENTS IN COASTAL SEDIMENT CORES

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INTRODUCTION

Weathering, transportation, deposition and diagenesis are the major stages in the sedimentary cycle. These stages may exert varied influence on the distribution and abundances of elements in sediments. The distribution and fractionation patterns of rare earth elements (REE) relative to local source may be related to these factors. The effect of weathering on the fractionation of REE is commonly associated with the preferential enrichment of light REE over the heavy REE in different soil and sediment horizons (Chaudhuri and Cullers, 1979).

In most parts of Antarctica, chemical weathering is not sufficiently important to cause major change in bulk composition of rocks and soils. However, in the maritime Antarctica, covering parts of the Antarctic Peninsula and the offshore islands, the climate is warmer and much greater quantities of free water are available. Soils in this part of the Antarctica are characterized by much greater predominance of cryoturbic processes as evidenced by the presence of patterned ground (Campbell and Claridge, 1987). Recently, it was reported that the main limitation on freeze-thaw weathering is not thermal but rather moisture, and that in ice-free areas close to the coastal regions soil formation and chemical weathering occurs to a greater extent than previously thought (Beyer *et al.*, 2000; Lee *et al.*, 2004).

The study of geochemistry of coastal sediments may provide insights into weathering processes in rocks and soils of maritime Antarctica. In fact, the fractionation patterns of REE between their source (rocks and soils) and their sink (sediments) may provide information about chemical weathering processes. Sediments provide a temporally integrated indication of the aquatic environment condition and act as a major reservoir for metals in aquatic environments. In this report, we made an attempt to understand trace and rare earth element behavior in three coastal sediment cores of Admiralty Bay, King George Island, Antarctica in order to verify some particularities of the sedimentary cycle in polar environments.

Admiralty Bay is a fjord in the King George Island, which is located approximately at 63°S in the South Shetlands Islands (Fig. 1). This bay has an area of 131 km²

and maximum depth of 530 m (Racuzza-Suszczenski, 1980). The South Shetlands Islands expose volcanic and plutonic rocks of Early Cretaceous to Early Miocene age, which are related to the subduction of the SE-Pacific oceanic crust underneath the Antarctic Continent. The South Shetland Islands receive larger amounts of rainfall than the eastern and southern regions of the Antarctica Peninsula (Pichlmaier *et al.*, 2004), so chemical weathering should be more important too. Mafic volcanic rocks (*i.e.* basalts, basalt-andesites, and andesites) are the dominant lithologies (Machado *et al.*, 2001).

MATERIALS AND METHODS

Three short sediment cores (up to 25 cm long) (MP- Macchu Picchu; BP- Botanic Point; and, CF- Comandante Ferraz Station) were collected with a box-corer in the coastal region of Admiralty Bay in January of 2004 during the XXII Brazilian Antarctic Expedition in a water depth of 30m (Fig. 1). These cores were sliced immediately after its collection. Redox potential and pH were measured *in situ* with portable electrodes in samples collected with the same box-corer, but in different layers (Fig. 2). In the laboratory, samples were lyophilized and ground for chemical analysis. Organic matter (OM) was determined by calcination (450°C, 24 hours), and fine-grained sediment (<0.062 mm) percentage was obtained after mechanical separation.

Trace and Rare Earth Elements (REE) were determined by Instrumental Neutron Activation Analysis technique (INAA). Approximately 150 mg of the sediment (duplicate samples) and about 120 mg of reference material were accurately weighed and sealed in pre-cleaned double polyethylene bags. Single and multielemental synthetic standards were prepared by pipetting convenient aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman n° 41 filter paper. Sediment samples, reference materials and synthetic standards were irradiated for 16 hours, under a thermal neutron flux of 10¹² n cm⁻¹ s⁻¹ in the IEA-R1m nuclear research reactor at IPEN – Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil. Two series of counting were performed: the first after one week decay and the second after 15-20 days. The counting time

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was 2 hours for each sample and reference materials, and half an hour for each synthetic standard. Gamma spectrometry was performed by a Canberra gamma X hyperpure Ge detector and associated electronics, with a resolution of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co , respectively. Data analysis was made by VISPECT program to identify gamma-ray peaks and by ESPECTRO program to calculate concentrations. Both programs were developed at the LAN/CRPQ, IPEN. The methodology validation was verified by measuring Buffalo River Sediment (NIST SRM 2704), Marine Sediment (PACS-2, National Research Council Canada) and BEN (Basalt-IWG-GIT) reference materials.

Recently, we suggested the use of Fe as geochemical normalizer to the detriment of Al for surface sediments of Admiralty bay because iron presented higher correlations with most elements (Santos et al., 2005). However, as we are now dealing with sediment cores, the redox sensitivity of iron (Wasserman et al., 2001) may interfere with its behavior and bias the interpretation of enrichment factor. Thus we used Th as a geochemical normalizer (Fig. 2). This element has been considered a reliable indicator of the contribution of terrestrial, crust-derived materials and is relatively immobile in aqueous solutions (Delwig et al., 1999).

RESULTS AND DISCUSSION

Results of geochemical determinations are presented in Tab. 1. Based on ratios between observed element concentrations and average earth crust content (Wedepohl, 1995), the elements measured in sediments of Admiralty Bay can be separated into four groups: (i) highly enriched elements ($EF > 2$): As, Br and Sb; (ii) slightly enriched elements ($1.1 < EF < 2$): Fe, Na, Nd, Sc, U, and Zn; (iii) non-enriched elements ($0.9 < EF < 1.1$): Eu, Hf, La, Lu, Sm, Tb, and Yb; and (iii) depleted elements ($EF < 0.9$): Ba, Ce, Co, Cr, Cs, K, Rb, and Th.

Approximately 8% of organic matter and a large fraction of muddy sediments characterize all three cores under study. The MP core had the lowest content of fine-grained sediments (mean of 77%), while CF and BP cores had means of 91 and 96% of fine-grained sediments, respectively. This difference between grain size distribution may be very important for understanding geochemistry of coastal sediments, since clay minerals are a major carrier of trace metals and REE in sediments.

The sediments of Admiralty Bay had a slightly alkaline pH (6.98 to 7.54), with a negligible depth-related variability. On the other hand, we found some strong gradient of Eh within the sedimentary environment of Admiralty Bay (Fig. 2). As expected, higher Eh values were found in surface layers. The lowest Eh value (-407 mv) was observed in the 8-10 cm layer of MP core, indicating a quite reducing environment. Even though Eh measurements in sediments should be considered semi-quantitative data due to large variability usually observed within the same sample, our results seem to represent well the general conditions of the sedimentary environment.

To access the possible occurrence of recent diagenetic processes in Antarctic sediments, we compared the profiles of some redox-sensitive elements (such as Eu, Ce, and U) with the profile of redox potential. Europium may be used for this kind of interpretation because it exists in the natural environment in both +2 and -3 oxidation states as apposed to generally +3 oxidation states for other REE. The preferential removal or adsorption of Eu^{2+} over other REE may explain Eu anomalies, and the Eu/Sm ratio is a measure of the variability of Eu anomaly. High Eu/Sm ratios may also indicate hydrothermal or volcanic activity, mainly along mid-ocean ridges and back-arc spreading centres (Delwig et al., 1999). The nearly constant Eu/Sm ratio within the sedimentary environment, which is similar to local rocks (see Lee et al., 2004) indicates that diagenesis have not played a major role in determining Eu distribution patterns.

Ce is also a redox-sensitive element that could indicate if diagenetic processes are taking place. Ce^{3+} is oxidized to Ce^{4+} in the oxygenated environments and the Ce^{4+} tends to be more rapidly removed by particle scavenging than the other REE in the +3 oxidation state. As a consequence, fractionation of Ce relative to other REEs must occur (Nozaki et al., 2000). However, in spite of strong Eh gradients, Eu/Sm and Ce/Th showed little or unpredictable variability in all three sediment cores under study (Fig. 2), indicating negligible influence of redox potential on their behavior.

In BP and MP cores, U/Th ratios also did not showed some remarkable gradient, but we were not able to determine U in some samples of these cores. In turn, U/Th ratios in core CF decreased in upper layers (Fig. 2), probably as a response of a higher oxygenated environment. In fact, U enrichment has been related to depleted oxygen contents. Uranium is mobilized as U^{6+} in oxic conditions and precipitated as U^{4+} in reducing environments (Delwig et al., 1999).

A comparison with published REE data from geological units likely to broadly represent the major eroding rock types showed that some characteristics of source rock REE profiles could be recognized in our data from coastal sediments of Admiralty Bay. In Fig. 3 are showed the concentrations of REE in sediments and rocks of the King George Island normalized by average concentrations in the earth crust. Admiralty Bay sediments appear to be primarily influenced by the weathering of basaltic andesite 2 (BA2) and by lapilli tuff, to the detriment of granodiorite and basalt andesite 1 (BA1). Sediments from CF and MP appear to be more influenced by lapilli tuff weathering than sediments from BP, as evidenced by Nd concentrations (Fig. 3). BA 1 belongs to the tholeiitic basalt to basaltic andesite with positive Eu anomalies, whereas BA2 belongs to transitional basaltic andesite to andesite with negative Eu anomalies, being more distributed in the King George Island (Lee et al., 2004).

As a preliminary conclusion, comparisons with the potential source rocks of Admiralty Bay sediments suggest little alteration during diagenesis and sediment transport in



the coastal region of the King George Island, even though higher moisture content occurs in this part of Antarctica than in other areas. It is supported by studies in soils of the King George Island, where homogeneous REE distribution patterns suggest that the soil REE's were not affected much during weathering (Lee et al., 2004).

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Table 1: Mean and standard deviation of organic matter (OM), fine-grained sediments (<0.062), and elements in studied sediment cores. Values in mg kg⁻¹, except OM, <0.062, Fe, K, and Na, which are in %.

	CF core		MP core		BP core			CF core		MP core		BP core	
	Mean	SD	Mean	SD	Mean	SD		Mean	SD	Mean	SD	Mean	SD
<0.062	90.9	6.1	77.4	10.6	95.7	2.0	La	17.9	0.7	16.4	1.0	18.7	1.3
OM	8.0	0.9	8.3	4.5	8.3	0.9	Lu	0.4	0.2	0.4	0.1	0.3	0.1
As	17.0	6.9	16.6	2.3	4.5	0.8	Na	2.75	0.21	2.19	0.31	3.00	0.15
Ba	264	104	333	23	271	88	Nd	37.1	7.3	25.5	6.3	34.6	11.6
Br	79.2	18.1	49.9	9.7	54.9	15.6	Rb	60.2	11.5	77.5	14.8	50.9	15.1
Ce	44.4	1.6	41.6	1.7	48.8	1.9	Sb	0.8	0.2	1.0	0.2	0.4	0.1
Co	17.0	0.7	19.4	0.9	21.6	0.7	Sc	23.3	0.9	22.1	0.9	22.9	0.7
Cr	28.7	7.1	21.6	2.1	40.0	3.5	Sm	5.5	0.2	5.1	0.2	5.9	0.2
Cs	3.1	0.3	3.1	0.4	2.4	0.4	Tb	0.6	0.2	0.8	0.1	0.5	0.3
Eu	1.4	0.1	1.2	0.1	1.5	0.1	Th	4.7	0.3	4.2	0.3	5.1	0.2
Fe	4.89	0.13	4.99	0.23	5.15	0.18	U	2.0	0.4	1.6	0.2	2.1	0.6
K	1.83	0.54	1.80	0.47	1.67	0.26	Yb	2.0	0.1	1.8	0.1	2.0	0.2
Hf	4.3	0.2	4.0	0.2	4.7	0.3	Zn	104.1	13.0	106.0	24.6	88.9	4.4

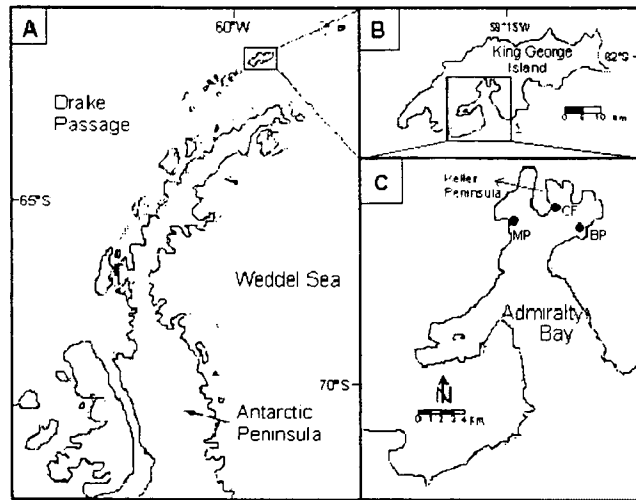


Figure 1: Study area and sampling points in Admiralty Bay, King George Island, Antarctica

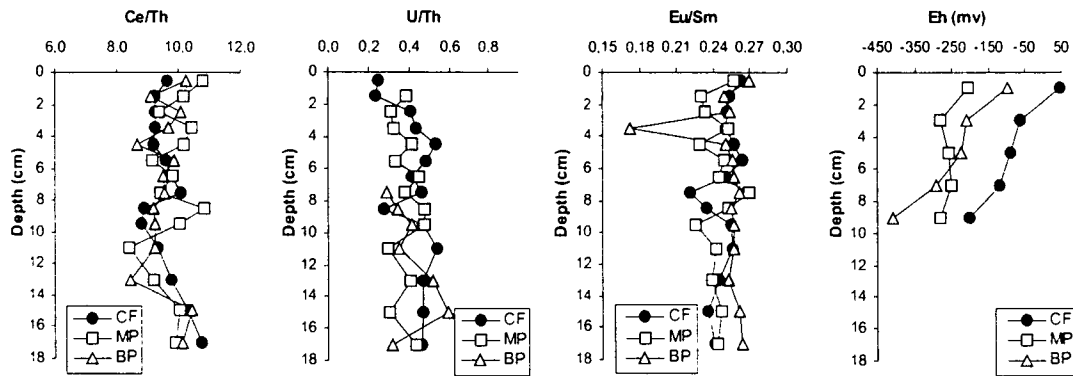


Figure 2: Vertical distribution of Eh and Ce/Th, U/Th and Eu/Sm ratios in coastal sediment cores of Admiralty bay.

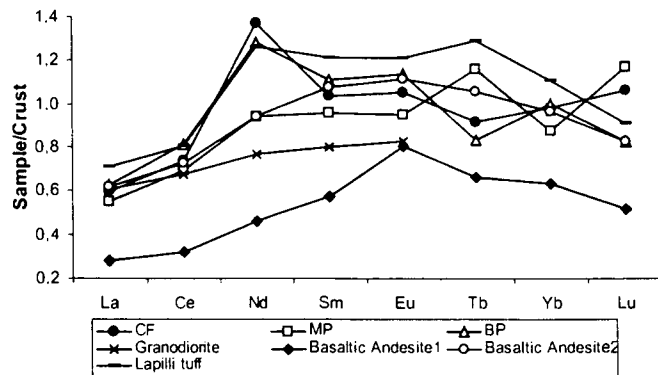


Figure 3: Concentrations of REEs in sediments and rocks (Lee et al., 2004) of the King George Island normalized by average concentrations of the earth crust (Wedepohl, 1995).