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REE enrichment in Havana Bay surface sediments using INAA

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Abstract Rare earth elements (REE) levels in Havana bay surface sediments are determined by instrumental neutron activation analysis. REE contents follow the order: Ce > La > Nd > Sm > Eu, Yb, Tb, Lu. The results shows that REE content in the bay is site depended and suggest that an REE anthropogenic input into the bay occurred. The chondrite and upper continental crust-normalizations confirm the REE enrichment of the bay sediments, respect to the REE content in sediments from the Cuban northwestern coast.

Keywords REE · Sediments · INAA · Havana · Cuba

Introduction

Rare earth elements (REEs) are interesting because of their minimal fractionation in the weathering, transporting and sedimentary processes and potential environmental problems as a result of their widespread use in agriculture and industry [1]. Many types of human activity, such as fossil-fuel combustion, waste incineration, metallurgic processes, etc., cause REE emissions to air, soil and water [2]. When these kinds of industries are in the surrounding of a practically isolated marine ecosystem, its sediments most likely should be polluted by REEs from such activities [3].

Havana Bay is the main Cuban harbor. It is a typical enclosed bay located at the north coast of west Cuba and has a total area of 5.2 km^2 and 18 km of internal coasts, an average depth of 9 m and a maximum depth of 15 m. It is characterized by a narrow entry channel, a central part and three coves: Atares, Guasabacoa and Marimelena. For many years, different rivers, several industries (including oil-fired power plants, oil refinery and metallurgic plants), drainage of the city and sewage systems (with high levels of organic material) spill wastes to this ecosystem, converting it in a considerable polluted bay. On the other hand, the demand for REEs and their compounds in modern industry and the rising mobilization of REEs in the environment, with the possibility of entering the food chain, highlights the problem of human exposure, thus requiring to monitor these elements in the environment, specially in sediments and suspended materials [4–6], in which they are mainly present at trace levels.

Instrumental neutron activation analysis (INAA), based on nuclear properties of the elements to be determined, is a powerful method for trace analysis of REEs in sediments [5–10]. The present study is part of a geochemical and isotopic analysis project on Havana Bay sediments using nuclear and conventional techniques. Particularly, INAA was employed to determine the REE levels in surface sediments from five zones of Havana Bay, and to study their behavior in this strong polluted ecosystem.

Experimental

Surface sediments were sampled using a Van Veen snapper in 14 points of the bay (Fig. 1) during the same day. All

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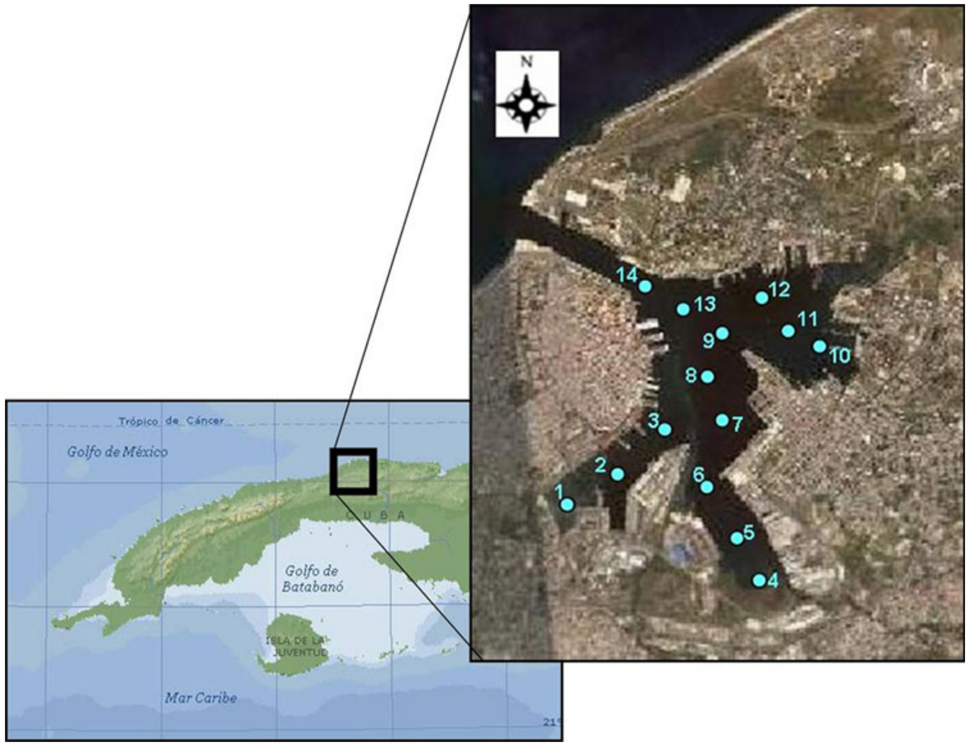

Fig. 1 Location of the studied stations in the Havana Bay

samples were dried at 50 °C. Large rock debris; mollusk skeletons and organic debris were removed before sieving. The fraction smaller than 1 mm was ground to a fine powder (<63 μm) in an agate mortar. The pulverized samples were newly dried at 50 °C until obtaining a constant weight.

For INAA, nearly 100 mg of each sample (in duplicate) and standards were irradiated during 8 h inside the thermal neutron flux ($\Phi_{th} = 8.3 \times 10^{13}$ n cm^{-2} s^{-1}) of the IEA-R1 reactor at the Institute of Nuclear and Energetic Inquiries (IPEN) of Sao Paulo, Brazil [11]. The reference certified samples GS-N and BE-N, developed at IPEN, were used as standards. In order to guarantee the determination of the largest quantity of the REEs, two series of measurements were carried out: one after 5 days, the other after 15 days of cooling time. The measurement times oscillated between 1 and 2.5 h. The spectra were collected by Canberra HPGe detector (70 cm^3, FWHM = 1.90 keV for 1332 keV) and processed using the VISPECT code developed at IPEN.

The accuracy was evaluated using the SR criterion, proposed by McFarrell et al. [12]:

$$SR = \frac{|C_X - C_W| + 2\sigma}{C_W} \times 100\%$$

where C_X is the experimental value, C_W the certified value and σ is the standard deviation of C_X. On the basis of this criterion the similarity between the certified value and the analytical data obtained by proposed methods is divided into three categories: SR ≤ 25% = excellent; 25 < SR ≤ 50% = acceptable, SR > 50% = unacceptable. The analysis of five replica of the CRM IAEA-SL-1 [13] is presented in Table 1. All REEs determined by INAA are "excellent" (SR ≤ 25%) and the obtained results show a very good correlation ($R = 0.9999$) between reported and measured contents.

Table 1 INAA of CRM IAEA-SL-1 (mean ± SD, $n = 5$, in mg kg^{-1}) and SR values

REE	$C_{measured}$	$C_{reported}$	SR (%)
La	51.4 ± 0.9	52.6 ± 3.1	6
Ce	118 ± 1	117 ± 17	3
Nd	44.5 ± 0.2	43.8 ± 3.8	3
Sm	8.7 ± 0.7	9.25 ± 0.51	21
Eu	1.51 ± 0.01	1.6[a]	7
Tb	1.5 ± 0.1	1.4[a]	21
Yb	3.5 ± 0.2	3.42 ± 0.64	18
Lu	0.51 ± 0.04	0.54[a]	20

[a] Non-certified elements in SL-1

Results and discussion

The samples were divided in five groups based on its location: the three bay coves [Atares (st. 1–3), Guasabacoa (st. 4–6) and Marimelena (st. 10–12)], the central part of the bay [Bay center (st. 7–9)] and the Bay channel

Table 2 Average concentrations[a] of REEs measured by INAA in different parts of the Havana bay (in mg kg^{-1})

Location	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Atares	9.7 ± 1.1	21 ± 4	12 ± 2	2.3 ± 0.5	0.6 ± 0.1	0.31 ± 0.01	1.3 ± 0.3	0.17 ± 0.04
Marimelena	12.9 ± 2.2	25 ± 3	16 ± 2	2.7 ± 0.2	0.7 ± 0.1	0.24 ± 0.02	1.2 ± 0.1	0.21 ± 0.02
Guasabacoa	10.0 ± 1.4	23 ± 3	14 ± 2	2.8 ± 0.3	0.7 ± 0.1	0.27 ± 0.07	1.3 ± 0.2	0.16 ± 0.04
Bay center	10.6 ± 0.4	24 ± 2	17 ± 2	2.9 ± 0.2	0.7 ± 0.1	0.30 ± 0.08	1.3 ± 0.3	0.22 ± 0.02
Bay channel	19.5 ± 1.1	33 ± 3	22 ± 8	2.7 ± 0.4	0.6 ± 0.1	0.29 ± 0.05	1.1 ± 0.1	0.18 ± 0.01
Cuban NW coast [14]	5	12	8	2	0.2	0.1	0.7	0.08
Upper continental crust [15]	32.3	65.7	25.9	4.7	0.95	0.5	1.5	0.27
C1 Chondrites [16]	0.236	0.619	0.463	0.144	0.0547	0.0353	0.166	0.0245
Diamond harbor, India [17]	21.5	44	19.6	4	0.7	0.5	1.1	0.2
Sepetiba harbor, Brazil [10]	40.9	80.5	–	6.3	1.3	–	1.4	0.2
Denia harbor, Spain [18]	23	45	21.3	3.8	0.9	0.51	1.4	0.22
Shangai harbor, China [19]	66	120	49	9	1.47	1.2	2.9	0.47

[a] Mean ± SD

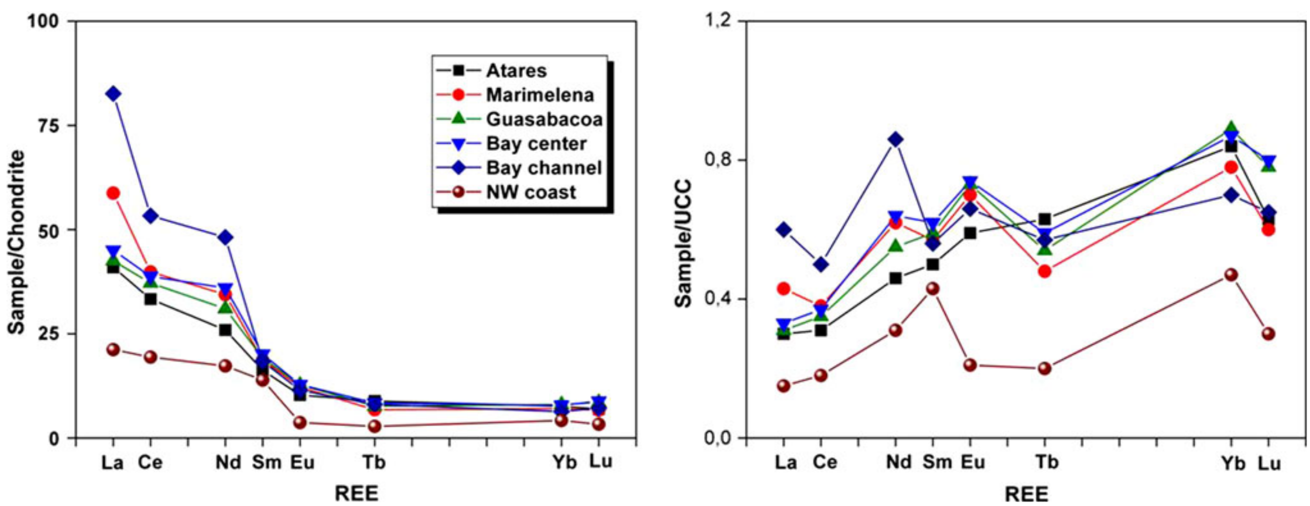

Fig. 2 Chondrite-normalized (*left*) and UCC-normalized (*right*) plots of the REE in sediments from Havana bay and Cuban northwestern coast

(st. 13 and 14). The first-time reported concentrations for an important group of REE (Table 2) is a great contribution of INAA to knowledge of the Havana Bay surface sediments. In general, the REE content in sediments from the Havana bay is site-depended, but in all cases the contents of REEs follow the order: Ce > La > Nd > Sm > Eu, Yb, Tb, Lu. The highest REE content was determined in Bay channel sediments and lowest in Atares cove. That difference must be associated with the nature of the sewage drained in each bay part and with the sediments movement from the coves to the bay channel [20].

Chondrite-normalized [16] distribution pattern (Fig. 2, left) confirm the relative strong site dependence of the REE content in Havana bay sediments, especially for light REE (LREE: La → Nd), and shows a relative high LREE enrichment in bay sediments respect to the LREE content in sediments from Cuban northwestern coast [14]. On the other hand, upper continental crust (UCC)-normalized [15] distribution (Fig. 2, right) shows that REE enrichment in Havana bay respect to Cuban NW coast is not only for LREE, a for all ones.

Independently of the above mentioned enrichment, REE content in Havana bay sediments is lower than REE concentrations reported for other harbors in the literature (see Table 2). Hence, the identification of REE content drained by industries located around Havana harbour is needed, in order to establish the necessary emission control and stop the REE input into the bay.

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