Geoquímica de Elementos Terras Raras (ETRs) como indicadores da proveniência dos sedimentos de albufeiras dominicanas

Geochemistry of Rare Earth Elements (REE) as a fingerprint of sediment provenance in Dominican Dam Reservoirs

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Resumo: A composição geoquímica dos elementos terras raras (ETRs) dos sedimentos depositados em duas albufeiras dominicanas, nos solos e rochas das respectivas bacias de drenagem, foi estudada de forma a identificar as possíveis fontes dos materiais depositados. Os teores dos ERTs dos 3 componentes foram normalizados a NASC, e determinadas a razão ETRs leves/pesadas, as anomalias de Ce e Eu e parâmetros de fracionamento. Os dados apontam para uma nítida depleção de ETRs das fontes, um enriquecimento em ETR leves e em alguns elementos intermédios (Eu, Er), anomalias positivas de Eu e maioritariamente positivas de Ce, o qual representa o elemento com maior variação espacial e temporal. Os padrões de distribuição dos ETRs são notoriamenmte mais homogéneos nos sedimentos, revelando uma sedimentação uniforme e pouco variável entre períodos sazonais distintos, não possibilitando a definição de fontes para cada sector das albufeiras. Diagramas bi-variados entre parâmetros de fracionamento de ETRs leves-médias-pesadas onde se projectaram os dados referentes a sedimentos, solos e rochas, permitiram uma boa descriminação das principais fontes dos materiais depositados nestas albufeiras.

Palavras-chave: Análise geoquímica; Elementos terras raras; Proveniência de sedimentos; Albufeiras dominicanas

Abstract: The geochemical composition of rare earth elements (REE) in the bottom sediments from two Dominican reservoirs, in soils and rocks from respective drainage basins, was studied in order to identify the possible sources of the deposited materials. The REE contents of the 3 components were normalized to NASC, and the light/heavy REE ratio, the Ce and Eu anomalies and a few fractionation parameters were determined. The data point to a clear depletion of REE from the sources, an enrichment in light REE and in some middle elements (Eu, Er), positive anomalies of Eu and mostly positive of Ce, which represents the element with greater spatial and temporal variation, related to chemical variation of the environment. The REE distribution patterns are notoriously more homogeneous in sediments, revealing a uniform sedimentation over the reservoirs and between distinct seasonal periods, not allowing the definition of sources for each reservoir sector. Bivariate diagrams between the fractioning parameters of light-middle-heavy REE, where the data of sediments, soils and rocks were plotted, allowed a good discrimination of the main sources of the materials deposited in these reservoirs.

Keywords: Geochemical analysis; Rare earth elements; Sediments provenance; Dominican dam reservoirs

1. Introduction

The mineralogical and geochemical "fingerprints" of clastic sediments are mainly controlled by the characteristics of source rocks and by the climatic conditions of the drainage areas (Pang et al., 2018). The geochemically immobile elements transported as particulate load, as rare earth elements (REE), are usually studied as tracers for sedimentary sources (Taylor and McLennan, 1985). The key role of these elements to identify sediments sources is based on the supposition that they only suffer slight geochemical fraccionation during the weathering, transport and deposition processes and are high resistant to chemical mobilization, reflecting the mineralogical and geochemical signatures of the basin's rocks. During these processes they are mainly linked to finer particles and therefore, they are transported as suspended load in rivers, leaving bed-load depleted on them and they preferencially concentrated in lakes (Singh, 2009). The REE chemistry in lake's sediments results from a number of processes including (1) sediment provenance, (2) physical and chemical processes regulating the delivery and availability of dissolved and particulate REE from the source rocks and soils to the lakes and (3) the chemistry of the water from which the particles settle (Hanningan et al., 2010).

In this study, levels and distribution patterns of REE were used to identify the source of sediments deposited in two dam reservoirs in Dominican Republic.

2. Characterization of the area

The contiguous drainage basins of the two studied reservoirs, Sabana Yegua and Tavera, are characterizad by high diversity of igneous and volcano-sedimentary rocks with island-arc origin, ranging from ultrabasic to intermediate composition, detrital and carbonated sedimentary rocks. The main differences between both basins is that Tavera has a greater extension of tonalitic, basic and ultra-basic rocks while Sabana Yegua has a greater influence of volcano-sedimentary, carbonated and detrital rocks as sources (where most of its three tributaries, Río Yaquel del Sur, Río Grande o Medio and Río de Las Cuevas) are embedded.

3. Methodology

Rocks and soils (top 20 cm) representative of the dominant lithologies in the two basins, were sampled. In the reservoirs, bottom sediments were collected with a Shipeck type dredge in two distinct seasonal periods (after and before rainfall) at points distributed by the reservoirs in order to include the areas of influence of all tributaries and the higher hydrodynamic conditions.

For REE study (including lanthanides, Y, Sc and Hf), samples were fused with lithium metaborate and subsequently dissolved in a hydrochloric acid solution. Amost all interfering elements were eliminated by leaching the solution with hydrochloric and nitric acid gradient concentration, through glass chromatogra-phic columns filled with a strong acid cationic exchange resin. Concentrated solutions were analysed by ICP-OES. For quality control, all chemical procedures were tested with analytical replicates and Certified Reference Materials (CRMs) with an accuracy of R<5%.

To avoid the Oddo-Harkins effect, the contents of all REE were normalized to NASC (North American Shale Composite), following the values proposed by Taylor & MacLennan (1985). The quantification of all elements, the ratio between LREE (light REE: La-Sm) and HREE (heavy REE: Gd-Lu), REE fractionation parameters obtained through the correlation between the NASC normalized concentrations ($(La/Yb)_N$, $(La/Sm)_N$, $(La/Gd)_N$, $(Gd/Yb)_N$, anomalies of Eu (Eu/Eu*) and Ce (Ce/Ce*) and NASC normalized Spider diagrams of La-Lu series and elements with similar behaviour (Y, Sc, Hf), were used as a proxy to define the origin and sources of sediments.

4. Results and Discussion

Representative rocks of each basin were grouped according to their petrographic classification into ultrabasic, basic and intermediate igneous rocks, volcano-sedimentary, metamorphic and carbona-ted rocks. Between groups and within some groups, rocks have distinct patterns in the distribution of normalized contents of the

La-Lu series (Fig. 1), as well as in the values of the Ce and Eu anomalies and in the fractionation parameters. While Eu/Eu* is always positive, Ce/Ce* is very diverse ranging from negative anomalies in carbonate rocks (±0.2) to high positive values in metamorphic and in some basic and ultrabasic igneous rocks. This variation reflects the control of REE patterns by the chemistry of these elements at their source and the crystal-fusion balance that occur during rocks evolution (Rollinson, 1993).

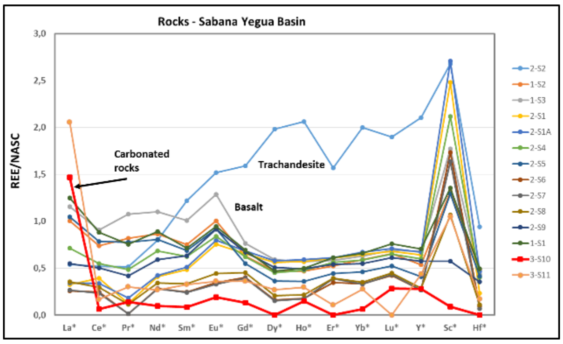

Fig.1 – NASC normalized REE patterns for rocks of Sabana Yegua basin.

The REE distribution in soils is widely diverse whithin and between each basin and rarely reflect the patterns of the source rocks, with the exception of soils on carbonate rocks which, although with a distinct distribution, inherited the negative Ce anomaly, though with higher values. In soils, REE concentrations result from the average content of mineral reservoirs of REE and minerals that adsorb REE from the environment. Although it is assumed that REE in sedimentary environments are immobile, studies developed by several authors (*in* Aide & Aide, 2012) concluded that there are numerous processes responsible for the migration of REE from soils, including biological and chemical processes and anthropic disturbances.

Due to theses conclusions and due to the variability of the REE patterns obtained, we consider the basin rocks as the best tracers for defining the sediments origin.

The chemistry of REE in sediments is consistent in space and time. There are no significant differences between different sampling points or sampling periods in the same sector of the reservoirs, reflecting a high homogeneity in the sedimentation process of these systems (Fig. 2).

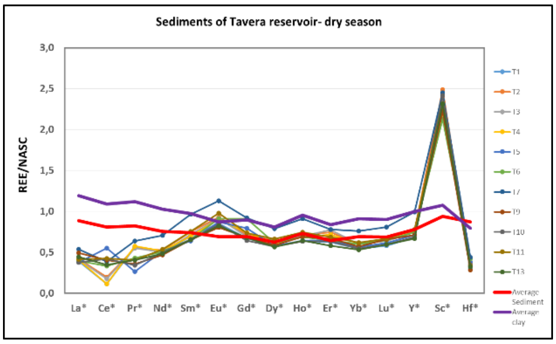

Fig.2 – NASC normalized REE patterns for sediments of Tavera reservoir in the dry season.

Only the SE sector of Sabana Yegua, under the direct influence of carbonate rocks, presents distint values concerning the elements contents, Ce and Eu anomalies and light-middle-heavy REE fractionation parameters, which are similar to the source rocks, denoting the inheritance of REE patterns in sediments from the rocks. Sediments of both reservoirs have a total value of REE between a narrow range of 61,6-89,4 mg/Kg in SY and 58,2-96,2 mg/Kg in Tavera, with a coefficient of variation (CV) of 9,9% and 14,3% respectively. Ce, Nd and La are the most abundant elements, representing 70-75% of ∑REE. Regarding the average values of the continental crust and an average sediment (Taylor and McLennan, 1985) the majority of sediments show a marked impoverishment in LREE (La-Nd), similar values in MREE (middle) and HREE, registering only a slight enrichment in Eu, Er and Lu and a notorious enrichment in Sc. The normalized values to NASC, with a ratio invariably lower than 1 in all elements, suggest the occurrence of impoverished sources in these elements in the drainage basins. These patterns show weak fractionation, with homogeneous values of the ratio LREE/HREE (4,13-5,51, CV: 8,52 % in SY and 3,77-6,16 in Tavera, CV: 15,4 %) and positive Eu anomalies (median values of 1,2 in both reservoirs). The levels and the anomalies of Ce are the parameters that present the greatest variability along the reservoirs and between the two sampling periods. This is the element most easily fractionated in sedimentary processes by oxidation from Ce^{3+} to Ce^{4+}, which can be separated as insoluble oxi- hydroxides.

In each reservoir, the bivariate diagrams where the values (∑REE, LREE/HREE, Ce/Eu anomalies, $(La/Yb)_N$, $(La/Sm)_N$, $(La/Gd)_N$, (Gd/Yb)) for the different groups of rocks, soils and sediments were plotted (Figs.3 and 4), allowed the discrimination of the lithological sources from the basins, responsible for the excessive sedimentation rates in these reservoirs.

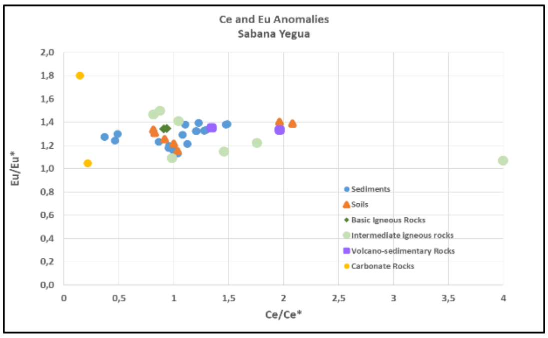

Fig.3 – Bivariate plot for Ce and Eu anomalies for Sabana Yegua basin.

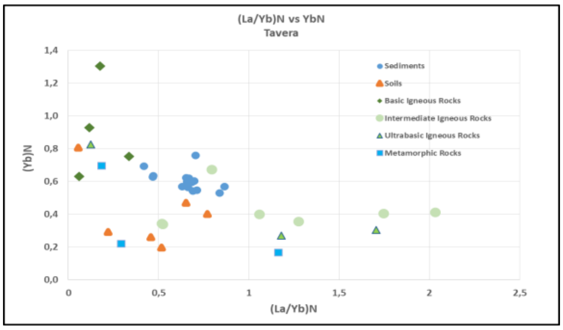

Fig.4 – Bivariate plot for $(La/Yb)_N$ and Yb_N for Tavera basin.

In all bivariate diagrams there is an overlap on the sediments projection, of data from some rock and soil groups, which represent the sediments sources.

(1) In Sabana Yegua, the sediments of the SE sector, under the influence of Río de Las Cuevas, are mainly feeded by the soils located in the most flattened areas developed on carbonate rocks, and by intermediate igneous rocks located in areas of greater slope in the NE area of this sub-basin. The rocks with the greatest influence on the sedimentation of the other sectors, are also located in steep slope areas: volcano-sedimentary rocks that emerge at the Northern edge of the Río Grande o Medio sub-basin and inter-mediate igneous rocks in a mountainous area in the central region of Río Yaque del Sur basin and soils located in flat areas in the vicinity of the lake.

(2) Tavera, with only one river to flow, Yaque del Norte, has contributions for some REE by lithologies dispersed in the sub-basins of the two tributaries, including tonalites and granodiorites in a flattened area close to the reservoir and ultrabasic and basic rocks in larger areas of steep slopes.

5. Conclusions

In this study, elements of the La-Lu series showed relative immobility and indepen-dence from the chemical conditions of the environment, which points to the importance of the REE analysis to define the sources of the materials deposited in these two reservoirs. This knowledge is particularly important to better control the environmenttal degradation of soils and the existence of intensive human activities, which may be the cause of the excessive siltation that annually occurs in these systems.

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