

Determination of the concentration of Ce, La, Sm and Eu in a phosphogypsum stack, in Imbituba city, Santa Catarina, Brazil

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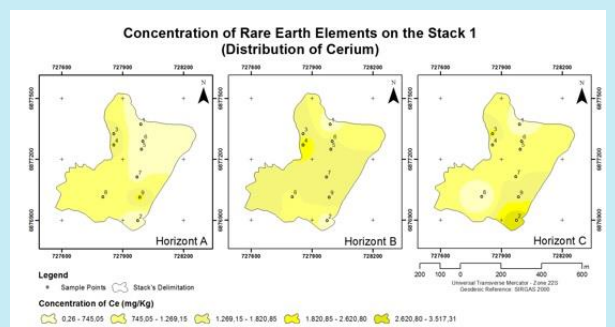
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ABSTRACT: Phosphate fertilizer industry produces phosphoric acid from phosphate rocks, and as a byproduct, it produces phosphogypsum, also known as agricultural gypsum. This material was stocked in open-air stacks near the producing units. In order to determine levels of rare-earth elements in phosphogypsum stacks, located in Imbituba, Brazil, samples of 2000 grams of phosphogypsum were collected in nine different points in stack 1. The concentration of rare-earth elements was determined through neutron activation analysis and results indicate significant values of rare-earth elements in the phosphogypsum from Imbituba, when compared to the values of the Earth's crust.



1. Introduction

Phosphogypsum is a byproduct of phosphoric acid industry and it comes from acid leaching of phosphate rock with water and concentrated sulfuric acid. Phosphogypsum is a calcium sulfate dehydrate, which physical and chemical characteristics are equal to natural gypsum. Although phosphogypsum is mostly composed of calcium sulfate dehydrate, impurities from the original phosphate rock can be identified in high levels. These impurities are redistributed between the phosphoric acid and the phosphogypsum, during the manufacture. The insoluble impurities (or solubilized in the acid medium) consist of chemical elements, such as metals, rare-earth elements, fluorides and radionuclides¹.

Rare-earth elements can enter into human organism by ingesting contaminated food and

inhaling particles in suspension. Most of rare-earth elements, which are ingested, were excrete, although a short part can enter the bloodstream and accumulate in different parts of human body per ion exchange processes².

An extensive volume of phosphogypsum generated annually by phosphoric acid production industries in world has been receiving attention of radiological and environmental protection agencies. In the Brazilian state of Santa Catarina, there is a stack of the material, located in the city of Imbituba, south of the state capital, Florianópolis. This material is currently commercialized and applied in apple and soybean crops. Some studies with Brazilian phosphogypsum have already been performed. However, there are no studies on phosphogypsum from this Brazilian State, and specially, on its toxicity by rare-earth elements.

This work aimed to quantify the presence of rare-earth elements (Sm, La, Ce, Eu) in phosphogypsum of Imbituba - Santa Catarina.

2. Materials and methods

2.1 Study site

Georeferenced samples of the PG (phosphogypsum) studied were collected in nine

points in PG stack 1 (Figure 1), in the city of Imbituba, southern coast of Brazilian state of Santa Catarina ($28^{\circ} 13' 17''$ S and $48^{\circ} 38' 21''$ W). In addition, samples were collected in the Referenced Area (AR), with the purpose of comparison related to the chemical composition of the local soil without human interference (background value).

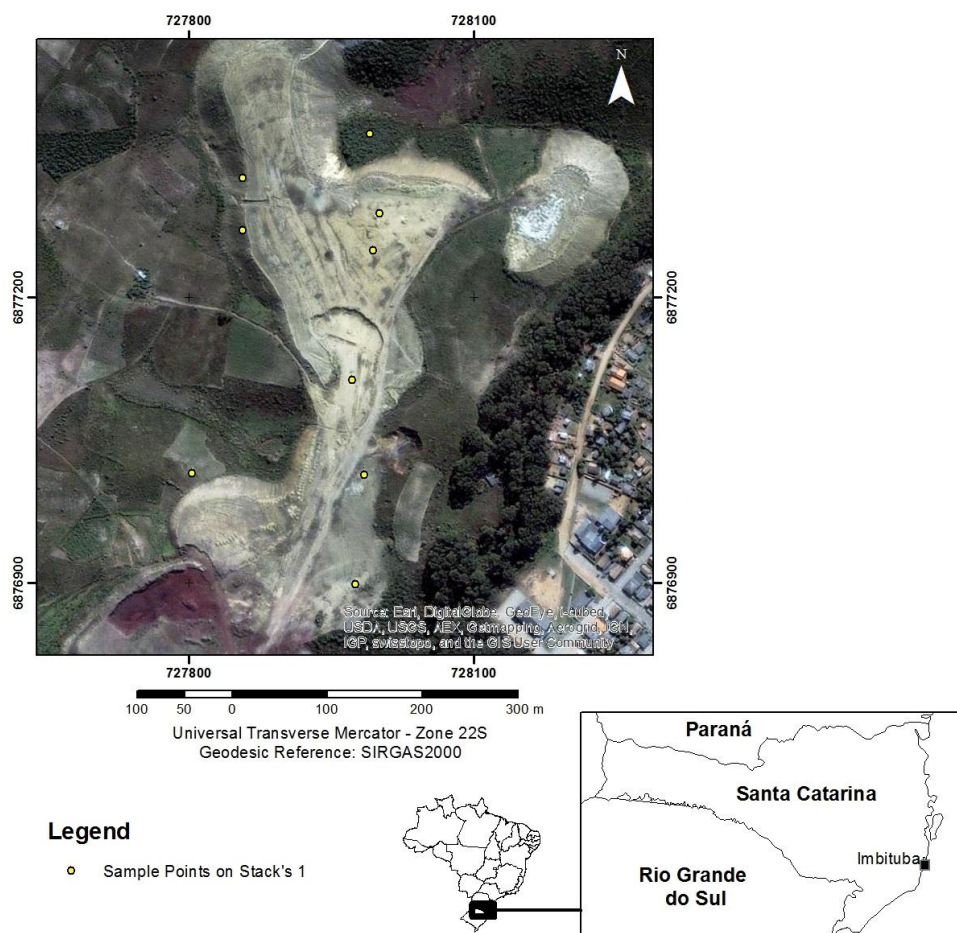


Figure 1. Georeferenced samples of PG.

2.2 Sample collection and preparation

Sampling procedures were managed in accordance to the Brazilian Association of Technical Standards (ABNT)³. The samples were collected in Engessul/Imbituba-SC, in May of 2008. The sampling procedures consisted on sample extraction, at different depths: 0 – 0.20 m (horizon A), 0.20 – 1 m (horizon B) and 1 – 2 m (horizon C) with the purpose of evaluation of the distribution of chemical elements according to the stack depth. The samples composed of 2000 grams

of phosphogypsum in each depth were conditioned in plastic bags previously identified and transported to the laboratory for posterior analysis. The soil samples followed the same procedures applied to the phosphogypsum.

All PG and soil samples were identified, grounded with a 2 mm mesh sieve at ambient temperature, to achieve a fine powder, and finally oven dried to constant weight.

2.3 Determination of rare-earth elements in the samples

To determine the levels of rare-earth elements in phosphogypsum and soil, the neutron activation analysis method was applied. Powder samples were homogenized in an agate mortar, individually. Around 200 mg of each sample was packed in polyethylene capsules using a four-decimal-place-graduated analytical balance. Capsules were sealed using a soldering tool with a graphite tip. Samples were irradiated for four hours in a thermal neutron flux of 10^{13} n cm⁻² s⁻¹ in the IEA-R1 nuclear reactor at Institute of Nuclear and Energetic Research (IPEN), São Paulo city, Brazil. In addition, “control” polyethylene capsules were also irradiated.

The standard used was the San Joaquin Soil (NIST 2709), that was prepared in the same way as samples with the view to guarantee the same geometries. To assess the data consistence and to guarantee the accuracy and reproducibility of the analysis, to each set of ten samples, one “control” sample and three samples of reference materials were analyzed.

The elements determined by this technique were Sm, Eu, La and Ce.

2.4 Statistical Analysis

Owing to the complexity and variability normally observed in environmental studies, it is common the use of multivariate statistical methods to differentiate and identify natural levels of heavy metals from anthropogenic contamination. With the view to verify parameters that contribute with the characterization and how they were related with the methods used, cluster analysis was performed using STATISTICA 7 software (StatSoft Inc.).

3. Results and discussion

3.1 Concentration of rare-earth elements

The REE (rare-earth elements) in phosphogypsum derive by its raw material (phosphate rocks). There were two kinds of phosphate rocks: the sedimentary and igneous rock. The ore matrix used in the acid production process is the source of REE in the phosphogypsum. Phosphogypsum generated in Imbituba-SC was composed by phosphate rocks from igneous origins. Stack 1 was formed by igneous phosphate ores from Araxá – MG.

Table 1 presents rare-earth concentration values found in phosphogypsum analyzed in present study.

Table 1. Concentration (mean \pm standard deviation mg kg⁻¹) of REE from phosphogypsum in samples from other sources.

Element	Russia ⁴	Brazil ⁵	Brazil ⁶	Brazil ⁷	Stack 1
Ce	1600	2574	956	1730	1233 \pm 326
La	1050	1300	1017	973	27 \pm 4
Eu	30.4	36	26	29	36 \pm 3
Sm	76	149	123	85	70 \pm 12

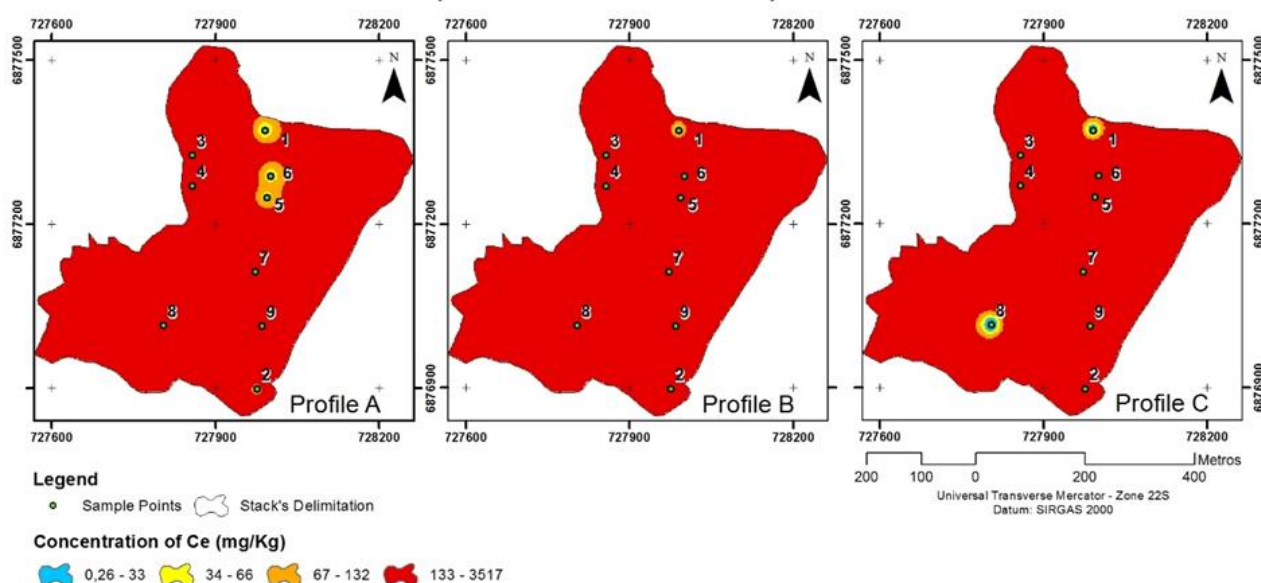
Results showed that for Ce there were no large variations in the concentration, whereas La has a lower concentration in relation to those found by other authors. Eu and Sm present values close to those found in phosphogypsum from other regions. The summation (Σ) of the total concentration of the REE (Ce, La, Eu and Sm) in the studied phosphogypsum was 1366.3 mg kg⁻¹.

Figures 2, 3, 4 and 5 show the distribution of REE in relation to the depth in phosphogypsum of Imbituba.

Figure 2 presents Cerium (Ce) results. In the Earth's crust, the mean concentration of Ce is 66 mg kg⁻¹, and in Chinese soils, the average concentration found in eight different types of soils was 86 mg kg⁻¹⁸. In Dutch soils, the maximum allowable concentration for Ce is 53 mg kg⁻¹⁹.

There are no established guidelines values for this element in Brazil. Although, in this study,

stack 1 has Ce values much higher than the allowed.



According to Lapido-Loureiro *et al.* (2008)¹⁰, apatite, along with its varieties, form a relevant group of minerals. The Ca^{2+} can be replaced, principally, by rare-earth element light in igneous apatite and rare-earth element heavy in sedimentary origin. The results confirm this data, since stack 1 was formed by igneous rocks that were enriched with Cerium.

Comparing the values of Ce in igneous phosphate ores¹¹, the concentration in stack 1 was in the range for the apatite in Norway (494.4–5352.9 mg kg^{-1}), which confirms, again, the high concentration of REE in igneous rocks.

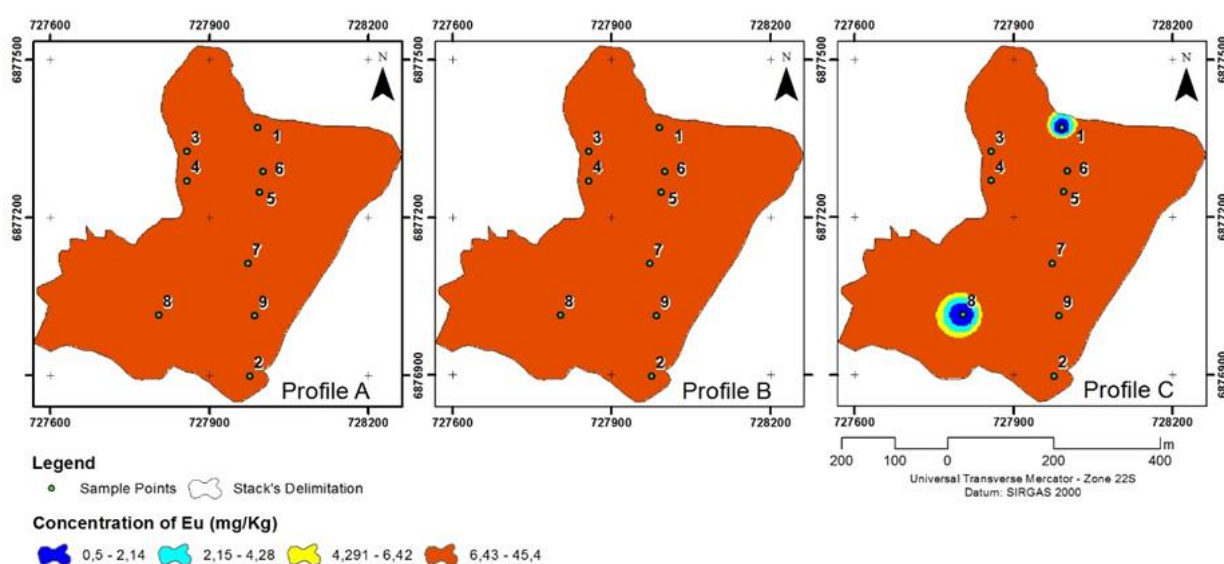


Figure 3 presents results for Europium (Eu). Eu is an element not found in nature as a free element and it is difficult its separation. The oxidation states

are +3 and +2 and Eu was found in ores containing small amounts of all REE. In the Earth's crust, the mean concentration of Europium is about 2.14 mg

kg^{-1} ¹². The average value obtained in stack 1 was 35 mg kg^{-1} , higher than the determined for the crust and soil, but still in the concentration range found in igneous phosphate rocks $21.5 - 73.7$ ¹¹.

Evaluating the Eu concentration, according to the depths, it is possible to observe that the values

decreased as the depth increased; that is, the horizons B and C presented lower concentration of the element.

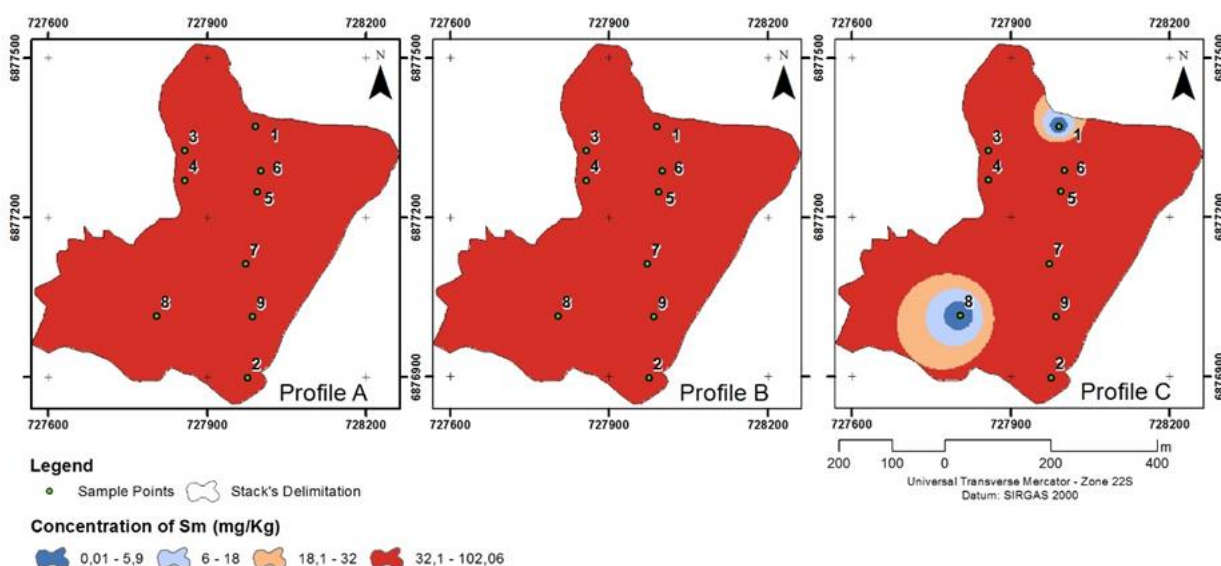


Figure 4. Distribution of Samarium on the stack 1.

Figure 4 presents results for Samarium (Sm). In stack 1, the average concentration of Sm found in phosphogypsum was 70 mg kg^{-1} , less than mentioned by Ihlen *et al.* (2014)¹¹, that found a concentration in the range of $86.3 - 323.3 \text{ mg kg}^{-1}$ in igneous phosphate rocks. Presumably, this is

related to the redistribution of Sm that has undergone chemical processing of phosphate rock.

Noticing the concentration over the depth: surface samples showed the highest concentration of this element and samples from the third depth, the lowest level.

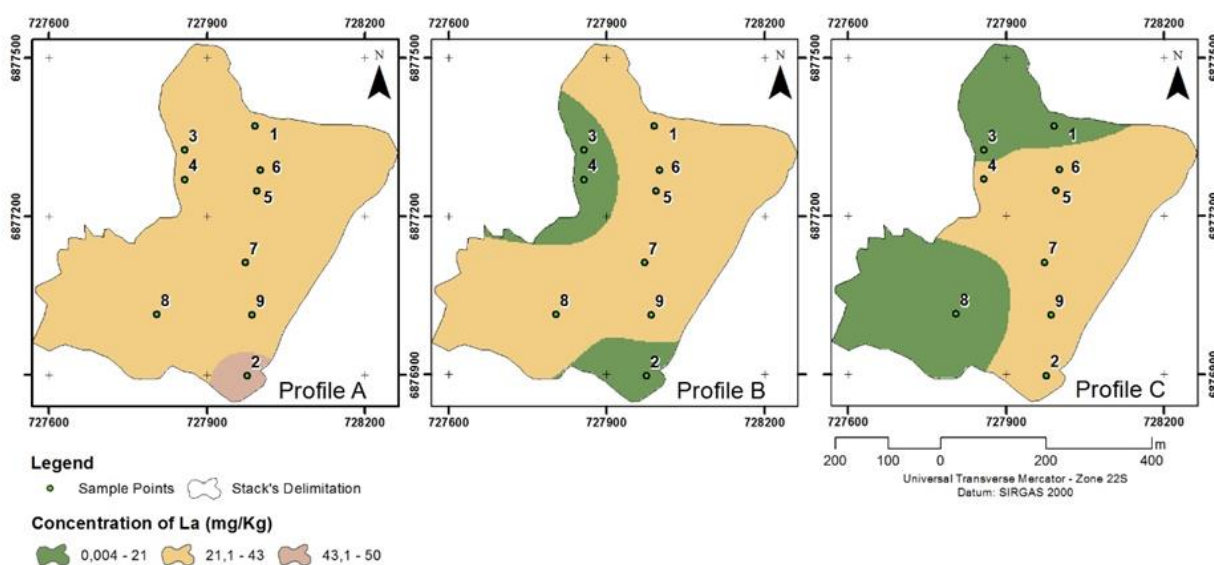


Figure 5. Distribution of Lanthanum on the stack 1.

Figure 5 shows results for Lanthanum (La). In the Earth's crust, the mean value found was 43 mg kg⁻¹¹³. Concentration found to La, in samples from stack 1, were considered intermediate, when compared to the values determined for igneous rocks and below, when compared to the global average. Furthermore, few samples of phosphogypsum collected in the second and third depth of the stack 1 showed the maximum concentration for La.

It was observed that La, Eu and Sm underwent little variation with depth, and Ce, in some points, presented a great variation; this is because REE in phosphogypsum samples were associated to the formation of carbonates, fluorides, sulfates and phosphates of these elements⁸.

The experimental results and the certified values are in Table 2.

Table 2. Concentration (mean \pm standard deviation mg kg⁻¹) of REE from different literatures, reference area and standard certificate

Element	Earth Crust ⁸	Referenced Area	San Joaquin Soil (Experimental Values)	San Joaquin Soil (Certified Values)	Sandy soil ⁷	Soil in Japan ¹⁴
Ce	66	0.14 \pm 0.01	0.044 \pm 0.001	0.042 \pm 0.001	21 \pm 1	33
La	35	14.5 \pm 0.3	0.026 \pm 0.001	0.023 \pm 0.001	3.0 \pm 0.3	15
Eu	2.1	5.1 \pm 0.3	0.011 \pm 0.001	0.009 \pm 0.001	<0.04	0.8
Sm	7	4.1 \pm 0.2	0.038 \pm 0.001	0.038 \pm 0.001	0.39 \pm 0.02	3.4

The results obtained by the evaluation of the influence of the phosphogypsum stacks to the surrounding soil (RA) were presented in Table 2 with other results from the literature.

The REE concentration results in RA soil samples were inferior to the values found in other researches, for the Earth's crust, with exception of element Eu, which presented higher concentrations.

In contrast, the RA soil showed heavy REE enrichment, indicating that the stacks have changed in some way the concentration of the elements in the soil under its influence.

Comparing the RA results to the soils found in other researches, it is possible to observe that the

Ce concentration was lower than in the soils from Japan and sandy soils. The La and Sm concentrations, however, were close to the values found in Japanese soils and higher than Brazilian sandy soils. On the other hand, the Eu had its concentration higher in the RA than in the other researches, which indicate that there was an increase of the element on this area.

3.2 Statistical Analysis – Cluster

Figure 6 shows the result of Cluster analysis using the software STATISTICA 7 (StatSoft Inc.).

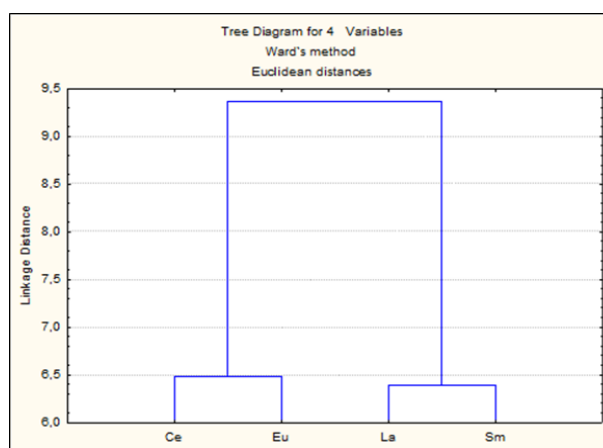


Figure 6. Cluster analysis.

It is possible to observe that there is the formation of two large similarity groups: first, composed by Ce and Eu, which presented much higher concentrations in the phosphogypsum than in the Earth's crust; and the second, composed by La and Sm, whose concentrations were closer to the results obtained for the Earth's crust.

4. Conclusions

The result obtained (Σ REE the order of 1366.3 mg kg⁻¹) indicated that the phosphogypsum produced in Imbituba has a high concentration of REE when compared with background values found in environmental samples. High concentration of rare-earths in phosphogypsum suggests that these elements may contaminate animals, plants, rivers, lakes and consequently humans during the ingestion of food grown on soils treated with this phosphogypsum.

Results showed a high concentration of Ce and Eu and a concentration below the global average of La when compared to igneous rocks from other regions. However, Eu and Sm presented values close to those found in phosphogypsum of other regions. This is due to the origin of matrix rock used in the processing, which may vary the concentration of REE in phosphogypsum.

5. Acknowledgments

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