DETERMINATION OF RARE EARTH ELEMENTS IN *Solanum lycocarpum* IN "CERRADO DE EMAS", PIRASSUNUNGA, SÃO PAULO, BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

In the present work, the concentration of rare earth elements (REE) in plant leaves of the species *Solanum lycocarpum* from "Cerrado de Emas", Pirassununga, São Paulo, and in the soil it has grown at, was determined by using Instrumental Neutron Activation Analysis (INAA). The obtained values for most of the light REE (La, Ce, Nd) were higher than the reference values for REE in plants. These results suggest that the light REE are more available in the soil than the heavy REE. The concentration of REE in the plant and the soil were normalized to chondrite contents, showing in the soil diagram a negative anomaly for the concentration of Eu and a positive anomaly for the concentration of Ce, which were not observed in the plant diagram.

I. INTRODUCTION

There is not much information so far about the concentration, behavior and absorption of the rare earth elements (REE) by plants from the soil [1], although they are considered to be the most adequate elements for investigation of the chemical evolution of the earth's crust. This is due to analytical difficulties in the determination of these elements, especially in biological samples, where they are found to be present many times in very low concentration values, just as ppb or ppt [2]. However, sensitive analytical techniques such as ICP-MS [3] and Instrumental Neutron Activation Analysis (INAA) [4] have proved their worth in such analysis.

In spite of the fact that some studies about the concentration of REE in plants are already reported in the literature [1], there is still little information referring to tropical species. In Brazil, Lima e Cunha *et al.* [5] have studied the species *Solanum lycocarpum* in the alkaline-ultramafic complex of Catalão I, Goiás. Ceccantini *et al.* [6], investigated the concentration of REE in different plant species related to the soil and underground waters in the alkaline-ultramafic complex of Salitre, Minas Gerais. These complexes, due to the particular mineralogy of the bedrock, show a high concentration of REE in the soil.

In a previous work, Piorino-Maria *et al.* [7] analyzed the species *Solanum lycocarpum* in the complex of Salitre. This typical Brazilian "cerrado" plant is widely distributed across the country, occurring in many alkaline-ultramafic complexes.

A significant difference in REE levels was found in the total REE concentration in the studied areas, of 600 to 6000 $\mu g.g^{-1}$ in the ashes, in Catalão I [5], and about 60 $\mu g\ g^{-1}$ in Salitre [7]. These results suggest different distribution patterns of REE in those plants as the substratum changes.

With the purpose of contributing for information about the REE concentration levels in tropical plants, and giving continuity to this study, the soil and plant leaves of *Solanum lycocarpum* from "Cerrado de Emas", Pirassununga, São Paulo , were analyzed. The soil of this area is originated from basic rocks, and do not present high levels of REE. Analysis of plant leaves and soil samples from two soil profiles were performed by INNA. The aims of this work are: a) provide the concentration values for REE in this species; b) compare the results to those previously obtained for the alkaline-ultramafic complexes of Catalão I and Salitre; c) evaluate the relations of REE concentration in plant-soil in the studied area.

II. EXPERIMENTAL

Preparation of elemental synthetic standards. Aliquots of standard solutions with well known concentrations of REE, were pipetted onto 1cm pieces of Whatman No. 40 filter paper, evaporated to dryness and packed in a polyethylene vial. These standard solutions of REE elements were prepared by dissolving their respective calcined oxides (Johnson Matlhey Chemical Limited) with nitric acid and then diluting with distilled water. In the case of cerium, a standard solution of this element provided from NIST was used. The precision and accuracy of the method were verified by the analysis of the reference materials NIST 1575 Pine Needles and BCR-CRM 101 Spruce Needles. The analysis of the materials Pine Needles and Spruce Needles has provided data for a work presented in a recent conference [8].

Sampling and analytical procedures. The plant material from the species *Solanum lycocarpum* was collected from Cerrado de Emas, Pirassununga, where the soil is originated from basic rocks, sandstones and tertiary sediments, which do not present a high concentration of REE. Sampling was performed in such a way that at least 1g of ashes was obtained, so 300 to 500g of fresh leaves (50-100g when dry) were collected. Five individuals of the species were sampled. The leaves were washed many times with abundant deionized water, dried (30°C), and homogenized in a blender. The grinded samples were put into ceramic capsules, dried (105°C for 24 h), weighed and ashed in a electric oven at 450°C for 12 h [9]. The soil samples were taken from two different profiles, in the same area where the plant material was collected. Five samples were taken from each profile at depths of 0, 25, 45, 85 and 100 cm. The samples were sieved in order to remove impurities like rock fragments or leaves and then homogenized for weighing and irradiation.

For the analysis by INAA, elemental synthetic standards and samples (plant or soil) were irradiated for 16 hours at a thermal neutron flux of 10^{12}n cm^{-2} s^{-1}, at the IEA-R1 nuclear reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP). The measurements of the induced gamma-ray activity were carried in a GMX hyperpure Ge detector (CANBERRA), connected to a S-100 multichannel analyser (CANBERRA) and to a personal computer. The resolution (FWHM) of the system was 1,90 keV for the 1332 keV gamma-ray of ^{60}Co. The gamma-ray spectra were processed using an in-house developed software. Two series of countings were performed, the first one five days after irradiation, for the determination of La, Sm and Nd, and the second one fifteen days after irradiation, for the determination of Ce, Eu, Tb, Yb and Lu. The counting times were about 3 hours.

III. RESULTS AND DISCUSSION

The results obtained for the REE contents in the studied plant leaves are presented in Table 1 (concentration ranges and mean of five individuals), together with the reference values [3] and the values previously obtained for the alkaline-ultramafic complex of Salitre [7]. It can be seen that for the light REE La, Sm and Nd the values obtained are higher than the reference values, and for the intermediate and heavy REE (Eu to Yb) the values obtained agreed with the reference values. This fact might indicate that there is a larger availability of the REE on the superficial layers of the soil, where the roots of the studied species are found. Moreover, in a study of the contents of REE in the species *Solanum lycocarpum* in the alkaline-ultramafic complex of Salitre, Piorino-Maria *et al.* [7] found higher concentration values. These results were already expected, since the concentration of REE in the substract of the studied area is actually lower.

The values obtained for the REE contents in the soil samples from the studied area are presented in Table 2. Owing to the great homogeneity of REE values in the two profiles studied, only the average values for this soil samples are presented.

TABLE 1. Concentration of Rare Earth Elements in *Solanum lycocarpum* Plant Leaves

Elements	Concentration range (ppm)	Mean values (ppm)	Dry weight (µg g^{-1})	Reference values (µg g^{-1})	Values from Salitre (µg g^{-1})
La	5.3-16.2	9±5	0.533	0.15-0.25	1.024
Ce	12-19	15±4	0.889	0.25-0.55	1.612
Nd	1.5-4.3	3±1	0.178	0.1-0.25	0.624
Sm	0.31-0.55	0.4±0.1	0.023	0.02-0.04	0.161
Eu	0.03-0.08	0.06±0.02	0.0035	0.005-0.015	0.028
Tb	0.025-0.027	0.026±0.001	0.0015	0.005-0.015	0.011
Yb	0.08-0.17	0.14±0.04	0.0083	0.015-0.030	0.013
Lu	----	----	---	0.0025-0.005	0.0039

(---) not detected

TABLE 2: Contents of REE (ppm) in Soil Samples from Different Depths

Horizons	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
0 a 25cm	7.6±0.5	29±3	4.3±0.7	0.93±0.04	0.15±0.02	0.14±0.04	0.92±0.16	0.14±0.01
25 a 45cm	7.5±0.9	30±3	4.1±0.9	0.92±0.11	0.15±0.02	0.14±0.04	0.91±0.21	0.14±0.02
45 a 85cm	7.5±0.9	32±3	4.1±1.0	0.91±0.11	0.17±0.02	0.16±0.04	1.0±0.2	0.15±0.02
85 a 1.0m	7.3±0.3	33±1	4.5±0.6	0.91±0.03	0.17±0.01	0.12±0.06	1.0±0.1	0.15±0.01
Mean values (a)	7.47±0.09	31±2	4.3±0.2	0.92±0.01	0.16±0.01	0.14±0.02	0.96±0.05	0.14±0.01

(a) N =10

The transfer factors for REE from soil to plant were calculated by dividing the REE concentration in the plant by the REE concentration in the soil [3]. The obtained factors ranges between 0,007 and 0.041, and were lower than the range reported by Markert and De Li [3] for a natural forest ecosystem (0,041-0,088). This is in agreement with the hypothesis of Markert [1] that the levels of REE in plants are independent from those of the pedologic substract; as a result, the higher REE level in the soil of "Cerrado de Emas" area induces low concentration factors for these elements in the plants.

For the comprehension of the diagnosis of REE the Masuda-Coryell diagram [10] is often used in geochemical studies. It consists in normalizing the REE contents in samples against the REE contents in chondrite meteorite, which are used as a reference. The concentration values of REE in chondrites used are those reported by Boynton [11]. The chondrite-normalized patterns of the species *Solanum lycocarpum* and of the mean soil value from "Cerrado de Emas" are shown in Fig. 1a and 1b, respectively. It can be seen that similar distributions patterns were obtained for the soil and the plant, presenting an enrichment of the light REE, indicating that they remain available to the plant in the more superficial soil layers, in contrast to the heavy REE, less absorbed. It can be observed that, in the soil diagram, there is a negative anomaly for the concentration of Eu and there is a positive anomaly for the concentration of Ce, which were not observed in the plant diagram. For Ce, it is probably due to the fact that, apart from the other light REE, Ce is found mainly as Ce^{4+}, in the form of a insoluble compound, not available to the plant. Consequently, Ce remains soluble only in the soil, as Ce^{3+}, keeping its abundance between the available REE, in a reducing atmosphere [5]. It is interesting to notice that the REE distribution patterns obtained for *Solanum lycocarpum* in different studied areas [5,7] were similar, indicating a typical REE absorption by this species.

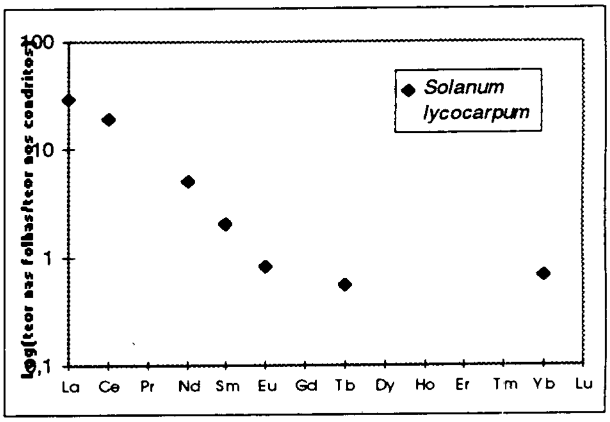

Fig. 1a. *Solanum lycocarpum* REE concentration values normalized to chondrite.

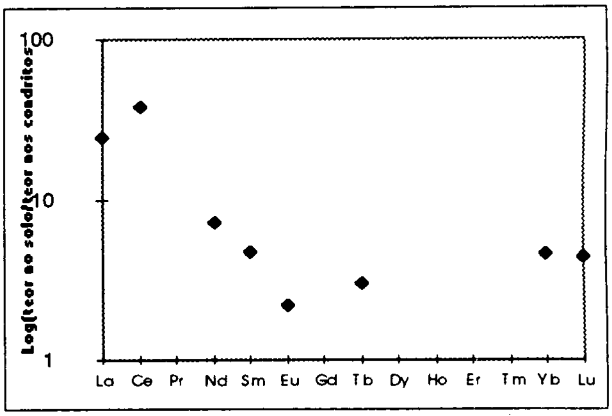

Fig 1b. Soil REE concentration normalized to chondrite.

CONCLUSIONS

The species *Solanum lycocarpum* in "Cerrado de Emas", Pirassununga, presented a higher light REE level than the reference values and concordant values for the heavy REE. The REE pattern obtained for the analysed plant was similar to the obtained for the soil, except for Eu and Ce, due to its non-availability to the plants. The soil-plant transfer factors found for the REE seem to indicate that the REE contents in the plants do not depend on the REE contents of the substract.

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