

Determination of the contents and distribution characteristics of rare earth elements in *Solanum lycocarpum* from tropical ecosystems in Brazil by INAA

Sh. P. Maria,¹ A. M. G. Figueiredo,^{1*} Gr. Ceccantini²

¹ Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP Caixa Postal 11049 – 05422-970 – São Paulo – SP – Brasil

² Universidade Federal do Paraná, Caixa Postal 19031 – 81531-970 – Curitiba – PR – Brasil

(Received November 22, 1999)

We have determined the concentrations of eight REE elements by instrumental neutron activation analysis (INAA) (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) in plant leaves of the species *Solanum lycocarpum*, a typical Brazilian “cerrado” plant widely distributed around the country, and in the soils in which they grow. Three different ecosystems were studied. Very similar chondrite normalized patterns were observed in the soil and in the plant, presenting an enrichment of the light REE, indicating a typical absorption of these elements by this species.

Introduction

There is presently not much information regarding 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 frequently found to be present in very low concentration values, such as $\mu\text{g}\cdot\text{g}^{-1}$ or $\text{ng}\cdot\text{g}^{-1}$.² However, sensitive analytical techniques such as ICP-MS³ and instrumental neutron activation analysis (INAA)⁴ have proved their worth in such analysis.

Despite the fact that some studies of the concentration of REE in plants are already reported in the literature,⁵ there is still little information referring to tropical species. In Brazil, LIMA E CUNHA et al.⁶ have studied the species *Solanum lycocarpum* in the alkaline-ultramafic complex of Catalão I, Goiás. CECCANTINI et al.⁷ have 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 show high concentration of REE’s in the soil.

We report an instrumental neutron activation analysis determination of the concentrations of eight REE elements (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in plant leaves of the species *Solanum lycocarpum*, a typical Brazilian “cerrado” plant widely distributed around the country, and in the soils in which they grow, in three different tropical ecosystems. The alkaline-ultramafic complex of Salitre is located in the west of the state of Minas Gerais. Due to the particular mineralogy of the original rocks, which contains perovskite, apatite, and calzirtite, these alterites present high contents of REE

(up to 5% $\Sigma\text{REE}_2\text{O}_3$). The vegetation is a mosaic of largely modified physiognomies of “cerrado”. “Cerrado de Emas” is situated in the Southeastern of Brazil, in Emas, Pirassununga, state of São Paulo. The soil of this area is a red latosol, with 40 to 60% of clay, originated from basic rocks. The vegetation is typical of “cerrado”. Pampulha lagoon is located in the urban region of Belo Horizonte, Minas Gerais, Brazil. The soil is originated from acid rocks, probably from elsewhere, since the lagoon has been artificially urbanized.

Experimental

Sampling and analytical procedures

Sampling was performed in such a way that at least 1 g of ashes was obtained, so 300 to 500 g of fresh leaves (50–100 g when dry) were collected. At least five individuals of the species were sampled, since significant differences in REE levels were observed from individual to individual, probably due to metabolic variations or to differences in the expansion of the roots.

The leaves were washed many times with abundant de-ionized water, dried (30 °C), and homogenized in a blender. The ground samples were put into ceramic capsules, dried (105 °C for 24 h), weighed and ashed in an electric oven at 450 °C for 12 hours.⁸ The soil samples were taken from the same area where the plant material was collected. The samples were sieved in order to remove impurities like rock fragments or leaves and then homogenized for weighing and irradiation.

Elemental synthetic standards of the REE and samples (plant or soil) were irradiated for 16 hours at a thermal neutron flux of $10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, at the IEA-R1 nuclear reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP).

* E-mail: grafigue@curiango.ipen.br

The induced gamma-ray activity were measured 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 five days after irradiation, for the determination of La, Sm and Nd, and the second fifteen days after irradiation, for the determination of Ce, Eu, Tb, Yb and Lu. The counting times were about 3 hours.

The interference factor due to the contribution of uranium fission products in the analysis of La, Ce, Nd and Sm was not determined, since this contribution was quite negligible.

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.⁹

Results and discussion

The results obtained for REE contents in *Solanum lycocarpum* plant leaves (mean of five individuals) and in the soil from the studied areas are presented in Table 1.

A noteworthy difference is found when we compare the results obtained for the total REE levels at the alkaline ultramafic complex of Catalão, Goiás (0.10 to $1520 \mu\text{g}\cdot\text{g}^{-1}$),⁶ at the alkaline ultramafic complex of Salitre, MG (0.08 to $31 \mu\text{g}\cdot\text{g}^{-1}$), at "Cerrado de Emas", Pirassununga, SP (0.03 to $20 \mu\text{g}\cdot\text{g}^{-1}$), and at Pampulha

lagoon, Belo Horizonte, MG (0.05 to $119 \mu\text{g}\cdot\text{g}^{-1}$). These results suggest different transfer factors of REE from soil to plant as the substratum changes. In Salitre, the transfer factors obtained changed from 0.0011 to 0.0032 , about ten times lower than the values reported in the literature, in the range of 0.041 to 0.088 .³ It can be explained by the fact that the soil of Salitre presents a much higher REE concentration than is usually found in soils. The relatively low concentration of REE in the plant in relation to the soil may be attributed to the low concentrations in the groundwater, verified in a previous work.⁷ This was also observed by EISEBUND et al. (see LIMA E CUNHA et. al.)⁶ in similar soils from Brazil, who attributed these concentration values to the low solubility of REE phosphates and hydroxides.

The REE concentrations in the plants from Pirassununga were lower than the ones found in Salitre, and the transfer factors ranged from 0.007 and 0.041 . These results confirm the idea of a different uptake of REE by the plant as the substratum changes, once the concentration of REE in the soil of Pirassununga is actually lower than the soil from Salitre. It is well known that pH is a significant factor for the availability of soluble ions to the plant. In general, tropical soils are acid. A decrease in pH will favor solution of the REE and their transport either as complexes or as free ions. An increase in pH can result mainly in the precipitation of the REE.¹⁰ The soil from Pirassununga presented a pH of 4.5 , lower than Salitre (5.0) and Pampulha lagoon (5.5). This fact may explain the similarity of REE concentration in the plant leaves from Salitre and Pirassununga, indicating a more effective uptake from the soil in Pirassununga.

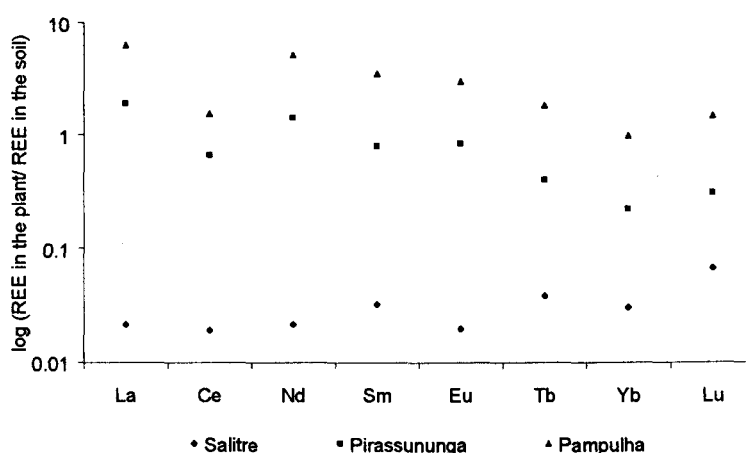


Fig. 1. Soil-plant transfer diagrams for the three studied sites

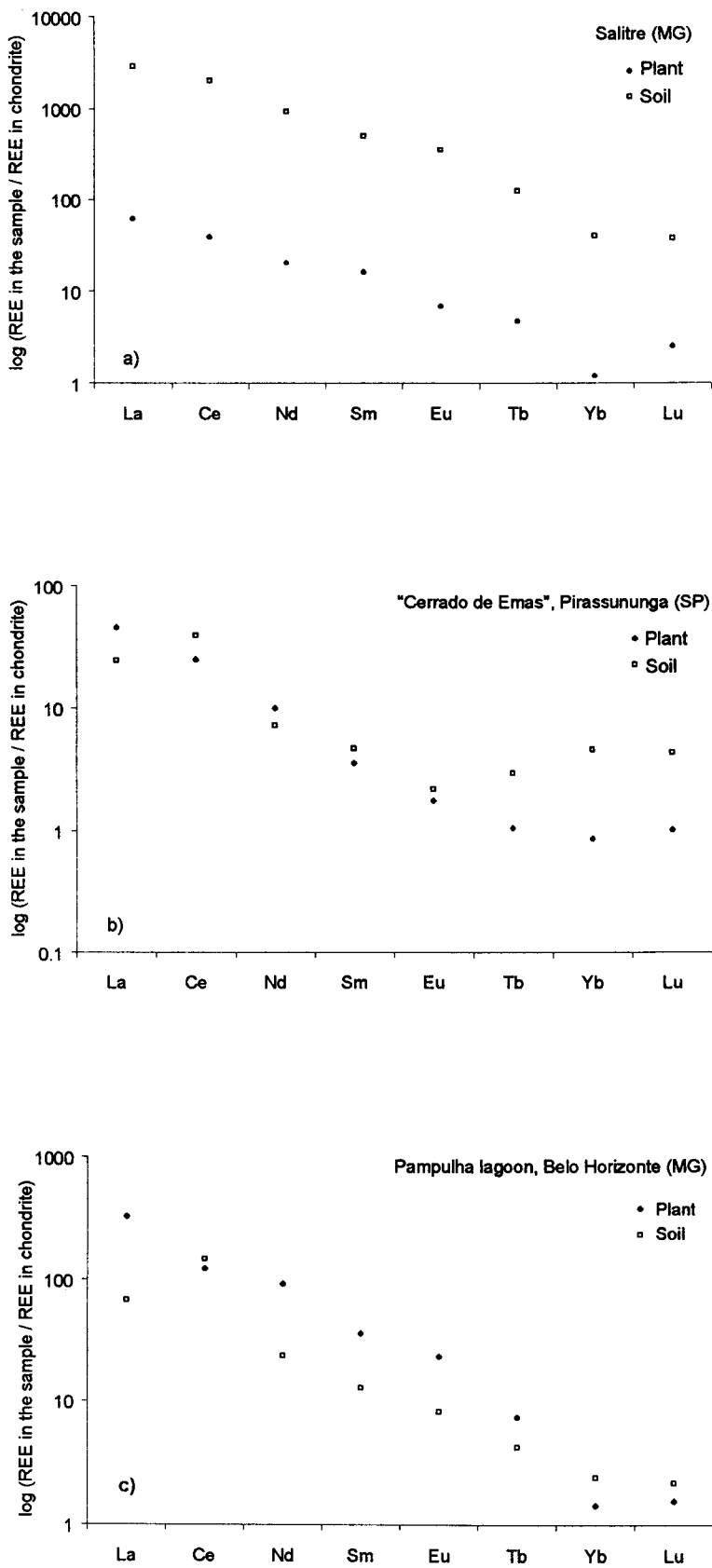


Fig. 2. Chondrite normalized patterns for *Solanum lycocarpum* and host soil from the studied sites

Table 1. REE concentration ($\mu\text{g}\cdot\text{g}^{-1}$) in *Solanum lycocarpum* plant leaves and average values in the soil, in different tropical ecosystems of Brazil

| Element | Alkaline-ultramafic complex of Salitre, MG | | "Cerrado de Emas", Pirassununga, SP | | Pampulha lagoon, Belo Horizonte, MG | |
|---------|---|-------------------|--|--------------------|--|--------------------|
| | <i>Solanum lycocarpum</i> | Soil (0–85 cm) | <i>Solanum lycocarpum</i> | Soil (0–100 cm) | <i>Solanum lycocarpum</i> | Soil (0–200 cm) |
| La | 19 ± 6 | 879 ± 18 | 14 ± 4 | 7.47 ± 0.09 | 102 ± 28 | 21 ± 5 |
| Ce | 31 ± 11 | 1613 ± 105 | 20 ± 4 | 31 ± 2 | 100 ± 14 | 119 ± 60 |
| Nd | 12 ± 2 | 555 ± 13 | 6 ± 2 | 4.3 ± 0.2 | 55 ± 8 | 14 ± 4 |
| Sm | 3.1 ± 0.1 | 96 ± 2 | 0.7 ± 0.2 | 0.92 ± 0.01 | 7 ± 1 | 2.5 ± 0.6 |
| Eu | 0.5 ± 0.1 | 26 ± 1 | 0.13 ± 0.04 | 0.16 ± 0.01 | 1.7 ± 0.4 | 0.6 ± 0.2 |
| Tb | 0.22 ± 0.08 | 5.8 ± 0.7 | 0.05 ± 0.02 | 0.14 ± 0.02 | 0.35 ± 0.09 | 0.20 ± 0.06 |
| Yb | 0.25 ± 0.06 | 8.3 ± 0.8 | 0.18 ± 0.05 | 0.96 ± 0.05 | 0.3 ± 0.1 | 0.5 ± 0.1 |
| Lu | 0.08 ± 0.04 | 1.2 ± 0.1 | 0.033 ± 0.008 | 0.14 ± 0.01 | 0.050 ± 0.009 | 0.07 ± 0.03 |

The REE levels obtained in the plant samples from Pampulha lagoon were higher than the ones found in the other sites studied. The transfer factors ranged from 0.61 to 5.02, much higher than the values reported in the literature.³ This fact could be explained by a larger availability of REE present in the soil to the plant. As Pampulha lagoon was artificially urbanized, the soil is not original from the area, and does not present a defined structure. Therefore, an association of soil characteristics to the availability of REE to the plant is difficult to establish. The higher uptake of REE in this area may be associated to the acid pH of the soil (5.5), which should make ions more available.

A plot of the REE concentration in the host soils divided by the REE concentrations in the plant for each studied area is shown in Fig. 1. The similarity between the diagrams points out a tendency for the absorption of the REE by the leaves of *Solanum lycocarpum*. In the case of Salitre, a higher transfer factor value was obtained for the heavy REE Tb, Yb, and Lu than for the light REE (La to Sm). This is due to the fact that, for Salitre, the difference between the light REE concentrations and the heavy REE concentrations is larger for the soil than for the plant.

For the comprehension of the behavior of REE in geochemical studies, the Masuda-Coryell diagram¹¹ is often used. It consists in normalizing the REE contents in samples against the REE contents in chondrite meteorite, which are used as a reference. The chondrite-normalized patterns of REE in *Solanum lycocarpum* leaves and in the host soil are shown in Fig. 2.

In the soil diagram from Pirassununga and Pampulha lagoon it can be observed that there is a positive anomaly for the concentration of Ce, which was not verified in the plant diagram. Also, in Fig. 1, for Pirassununga and Pampulha, a different behavior was observed for Ce. This is probably due to the fact that, apart from the other light REE, Ce is found mainly as Ce^{4+} , as insoluble compounds, not available to the plant.

It can be seen that similar distributions patterns were obtained for the soil and the plant in all the studied sites, 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, less absorbed REE. This behavior was also observed in *Solanum lycocarpum* leaves from Catalão, Goiás.⁶ The similarity between those distribution patterns indicates a typical REE absorption by this species, in spite of the significant differences in the substratum. Moreover, the fact that high concentrations of REE in the plant are related to the concentrations in the host soils is promising to evaluate the possible contamination of the environment by these elements.

*

The authors acknowledge FAPESP from Brazil for financial support.

References

1. B. MARKERT, *Phytochemistry*, 26 (1987) 3167.
2. B. MARKERT, H. PIEHLER, H. LIETH, A. SUGIMAE, *Radiat. Environ. Biophys.*, 28 (1989) 213.
3. B. MARKERT, Z. DE LI, *Sci. Total Environ.*, 103 (1991) 27.
4. Y. Q. WANG, J. X. SUN, H. M. CHEN, F. Q. GUO, *J. Radioanal. Nucl. Chem.*, 219 (1997) 99.
5. H. ICHIHASHI, H. MORITA, R. TATSUKAWA, *Environm. Pollut.*, 76 (1992) 157.
6. M. C. LIMA E CUNHA, M. L. L. FORMOSO, V. PEREIRA, *Geochim. Brasil*, 7(2) (1993) 101.
7. G. CECCANTINI, A. M. G. FIGUEIREDO, F. SONDAG, F. SOUBIÉS, *Proc. 3rd Intern. Conf. on Biogeochemistry of Trace Elements*, 1997, R. PROST (Ed.), INRA, Paris, No. 047 (CD ROM).
8. R. R. BROOKS, *Geobotany and Biogeochemistry in Mineral Exploration*, Harper & Row Pub., New York, 1972, p. 290.
9. C. N. MACHADO, S. P. MARIA, M. SAIKI, A. M. G. FIGUEIREDO, *J. Radioanal. Nucl. Chem.*, 233 (1997) 59.
10. P. HENDERSON (Ed.), *Rare Earth Element Geochemistry*. Elsevier. The Netherlands, 1984, p. 318.
11. A. MASUDA, *J. Earth Sci.*, 10 (1962) 173.