

CONTENTS

Rare earth elements and titanium in plants, soils and groundwaters in the alkaline-ultramafic complex of Salitre, MG, Brazil

G. CECCANTINI ¹, A.M.G. FIGUEIREDO ², F. SONDAG ³, F. SOUBIES ^{3,4}

¹ *Instituto de Biociências, Dpto de Botânica, CP 11461, 05422-970, São Paulo, Brasil*

² *Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Div Radioquímica, CP 11049, 05422-970, São Paulo, Brasil*

³ *ORSTOM, UR 12, TOA Dept., Laboratoire des Formations Superficielles, F 93143, Bondy Cedex, France*

⁴ *Université Paul Sabatier - UPS, Laboratoire de Minéralogie, Toulouse, France*

ABSTRACT

The contents of Rare Earth Elements (REE) and titanium in various species of plants, in groundwaters and in soils from the ultramafic complex of Salitre, MG, Brazil, were determined. Due to the particular mineralogy of the bedrock, REE and Ti present high concentrations in the soils. The transfer factors of the REE from soil to plants were calculated, giving values ranging from 0.0001 to 0.0028, much lower than the values reported elsewhere in Brazil. Furthermore, as suggested by other authors, the levels of REE in the plants appears to be independent from the REE contents in the soils. The concentrations of the REE in the plants, normalized to chondrites contents, show patterns similar to those of the soils. The patterns obtained for the normalized REE contents in groundwaters suggest an influence of the plant root activity leading to an enrichment in heavy REE. Some plant species show an accumulation of titanium and present concentration values about three times higher than the average content in plants cited in the literature. |

INTRODUCTION

In a recent past, little was known about the content of Rare Earth Elements (REE) in ecosystems. It was due to the very low concentrations of REE, mainly in biological samples,

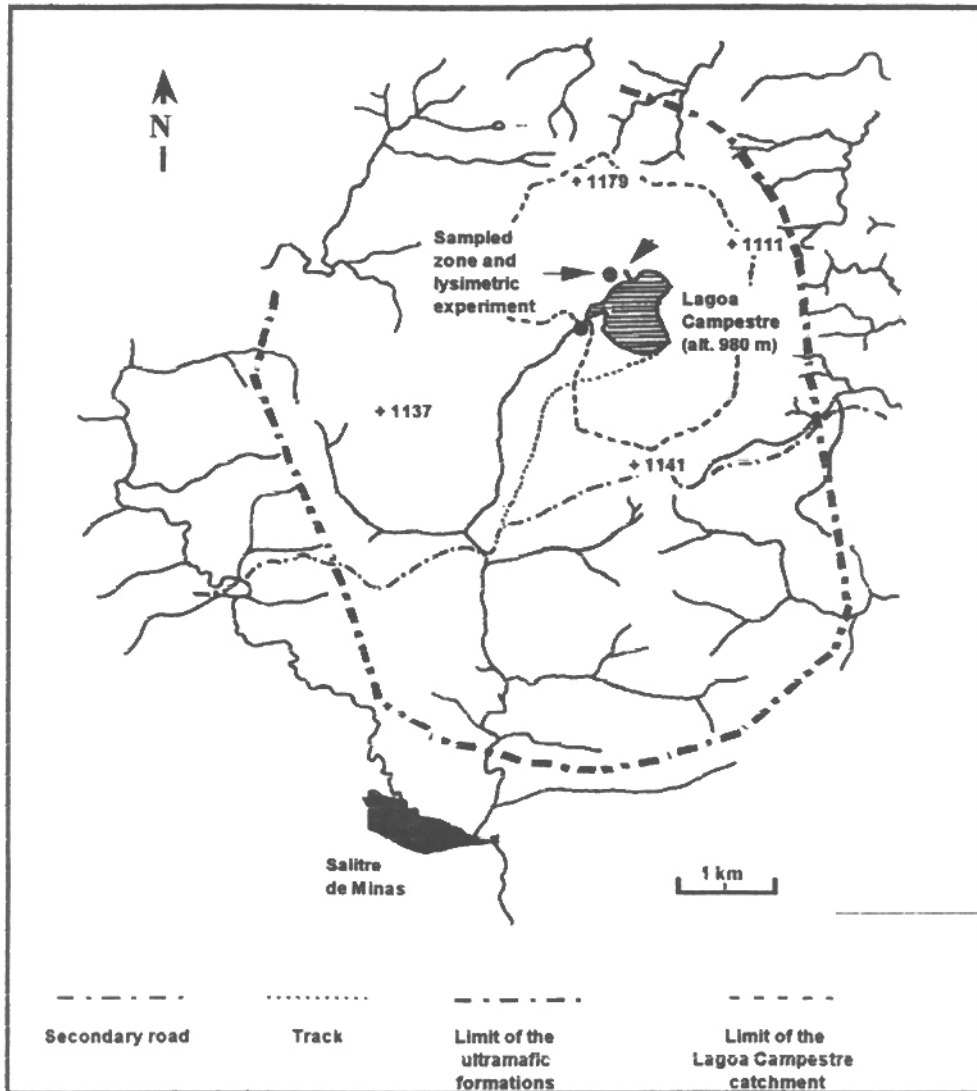
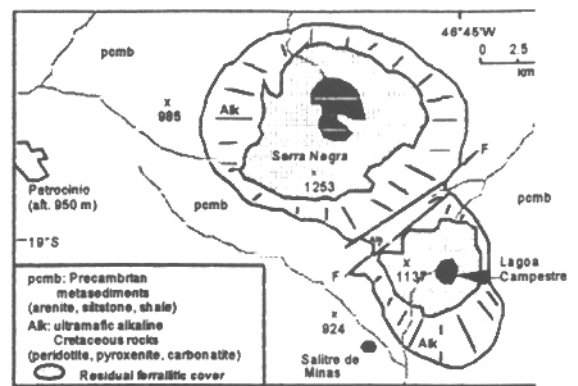
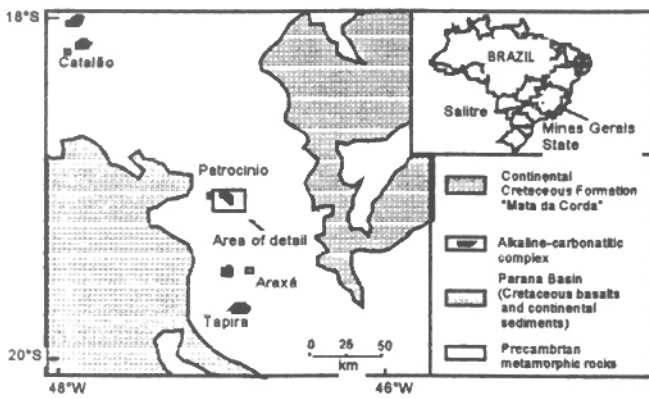


Figure 1. Localization of the Salitre area, geological context, drainage system, location of sampled zone and the lysimetric experiment (+1137= altitude in meters)

like plants, and to insufficient detection limits of the analytical methods (Brooks, 1972; Yliruokanen, 1975).

Since a few years, the development of highly sensitive analytical techniques allowed the precise and accurate determination of chemical elements which were formerly not detectable (Bowen, 1979), notably for the REE. Their concentration levels, behaviour and uptake by plants from soil have been investigated for the late few years (Caplan *et al.*, 1987; Markert *et al.*, 1989; Markert, 1992; Ichihashi *et al.*, 1992).

In tropical environments, little information is available about the concentration of REE in ecosystems, specially for regions with high REE levels in the soil. In Brazil, there is only one published study, for the species *Solanum lycocarpum*, in the ultramafic-alkaline complex of Catalão, GO, Brazil (Lima e Cunha *et al.*, 1993).

Several ultramafic complexes occur in the Alto Parnaíba area, in the West of Minas Gerais State, Brazil (Ulbrich & Gomes, 1981). One of these, the Salitre complex, presents REE and Ti at the percentage levels, due to its particular mineralogy. In the present work, the content of REE and Ti in leaves of various species of plants, in groundwaters and in soils from the region of Salitre were determined, aiming at the comprehension of the behaviour of REE and Ti in this ecosystem. The objectives of this work were: i) to verify if the plants growing in environments with high REE and Ti contents have higher concentrations of these elements than plants from non REE-Ti enriched soils; and ii) to evaluate the role of plant uptake on REE distribution pattern in groundwaters. For this research, the analytical techniques employed were Instrumental Neutron Activation Analysis (INAA) for the REE determination in soils and in plants, Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for the analysis of Ti, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for the groundwater analysis.

MATERIAL AND METHODS

Study area

The Salitre complex comprises mainly micaceous pyroxenites (“bebedourite”), peridotites and carbonatites. The intense leaching of these rocks originated a thick and loose lateritic cover (50-100+m), which covers the major part of the complex. This lateritic layer presents a central depression (“Lagoa Campestre”) partially filled by sediments and occupied

by a peaty lake (fig.1). The sampling area for leaves, water and soil is located about 30 m north of this lake.

Due to the particular mineralogy of the original rocks, which contains perovskite, apatite and calzirtite, these alterites present high contents in REE (up to 5% ΣR_2O_3), in TiO_2 (up to 30%), in ZrO_2 (up to 1 %) and Nb_2O_5 (up to 1 %). The original vegetation consists of semideciduous forest and brazilian savanna (“cerrado”). Nowadays, the cover is a mosaic of largely modified physionomies of “cerrado”, due to human activity (coffee and ranch). The most conspicuous features of this vegetation are the tortuosity of the trees and the leaf stiffness. The presence of thick barks and many kinds of underground organs make the trees resistant to fires that occurs very frequently in this vegetation.

The climate is tropical, characterized by a mean annual temperature of about 20 °C and a rainfall of $\pm 1,500$ mm; the length of the dry seasons reaches five months, from July to November.

Sampling and analytical procedures

Groundwater and soil

A pan-type lysimetric experiment (a trench about 3 m length, 1 m width, 1.5 m depth) was installed under a secondary “cerrado” cover, weakly disturbed by anthropic activity (fig. 1). The lysimeter has two types of collectors: 1). cylindrical lysimeters consisting of tubes of different lengths (10, 25, 45, 85 cm) containing undisturbed soil. 2). plate collectors, consisting of a flat recipient with a diameter of 25 cm, settled at the same depths as the former type. Both collectors were linked to funnels that lead the leachates to storage flasks. All parts of the lysimeter were made of plastic, to avoid contamination. On the one hand, the soil inside of the cylindrical lysimeters was isolated from the surrounding soil, so it was not penetrated by roots and the collected leachates represent 80-95 % of the rainwater drained vertically. On the other hand, the plate collectors do not prevent the root penetration and their adsorption activity, and collect only rapid circulating water, representing 2-10 % of rainwater (Chauvel *et al.* 1989, Sondag *et al.*, 1996).

Water sampling was performed during the dry season (June-November 1993) and at the end of the rain season (March 1994). The samples were filtered using a Millipore® 0.2 μm cellulose acetate filters and acidified with nitric acid for REE and trace element analysis. The REE were analysed by ICP-MS using ^{115}In and ^{187}Re as internal standards. The SLRS 2

standard water sample was taken as reference material using REE values obtained by neutron activation analysis.

Soils were sampled in a trench near the lysimetric experiment and in four other profiles around the "Lagoa Campestre". Four samples were taken from each profile at depths of 10, 25, 45 and 85 cm. Ti and other major and traces elements, including REE, were determined using ICP-AES after a mixed HClO_4 - HF digestion. REE were determined by INAA, as described below for the analysis of plants. The accuracy of the method was checked by the analysis of the geological reference materials UBN and GS-N. The precision ranges from 1.5 to 2.5 % for major elements and from 4 to 8% for traces elements.

Sampling and analysis of plant material

Plants were collected during the dry season (August 1993) in a area of about 100 m² around the lysimeter. The 12 most frequent species were chosen in a broad variation of tropical plant families (table 3). Sampling was performed in such a way that at least 1 g of ashes was obtained for each species, so 300-500 g of fresh leaves (50-100 g when dry) were collected. One or many individuals of each 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), weighted and ashed in a electric oven at 450°C for 12 h (Brooks, 1972).

For the analysis by INAA, aliquots of standard solutions with known concentrations of the analysed REE were pipetted onto a 1 cm² piece of Whatman® No. 40 filter paper and evaporated to dryness under an infrared lamp. Samples (200 mg) and standards were sealed in a plastic envelope and irradiated for 8 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 hyper-pure Ge detector, connected to an ADCAM 100 Multichannel Buffer (EG&G ORTEC) and to a personal computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma ray of ⁶⁰Co. The gamma ray spectra were processed using the program VISPECT, developed at IPEN by Dr. Denis Piccot, from Saclay, France. 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 15 days after irradiation, for the determination of Ce, Eu, Tb, Yb and Lu. The counting times were about 3 hours. The precision and accuracy of the method were verified by the analysis of the reference materials "Citrus Leaves" and "Pine Needles"(NIST).

RESULTS

The results obtained for the REE and Ti contents of different soil profiles from the region of Lagoa Campestre are presented in table 1. Owing to the great homogeneity of REE values in the different studied profiles, only the average values of these soil samples are presented.

Table 1. Average rare earth elements^a and Ti^b concentrations in soil profiles from the region of Lagoa Campestre; (N=20) (mg Kg⁻¹)

	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Ti
Soil content	879	1613	555	96	25	5.8	8.3	1.2	5.2
	± 18	± 105	± 13	± 2	± 1	± 0.7	± 0.8	± 0.1	± 0.2
Chondrites ^c	0.329	0.865	0.630	0.203	0.077	0.052	0.220	0.034	-

^a- INAA; ^b-ICP-AES, ^c-Boynton, 1984

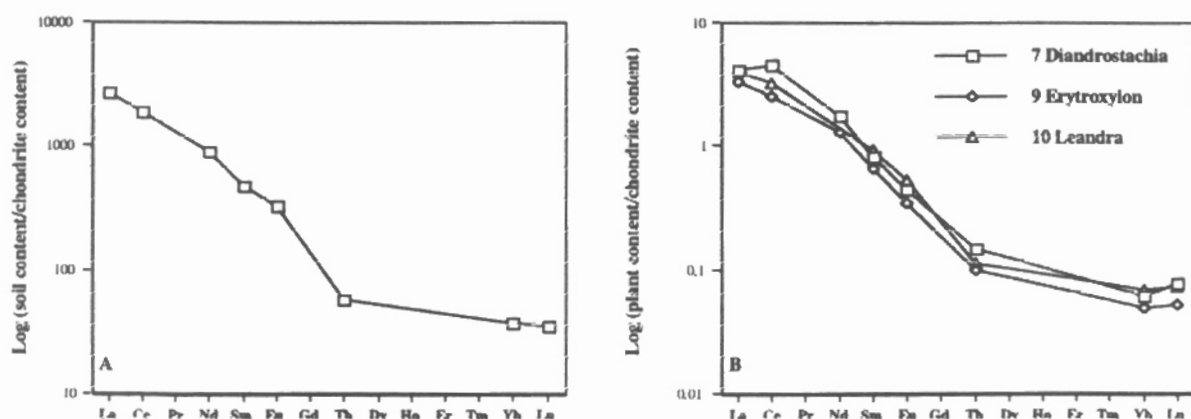


Figure 2. REE contents in soil (A) and plants (B) from Lagoa Campestre region normalized to chondrites content.

The high levels of REE and Ti in the study region is well reflected by the observed values.

In the table 2, the values obtained for the reference materials Pine Needles (NIST 1575) and Citrus Leaves (NIST-1572) are shown, along with the proposed values (NIST, Markert & De Li, 1991). The results are in good agreement with reference values. The reproducibility of the method was tested by six replicate analysis of the sample and the errors associated with the data represent one standard deviation. The elements Tb and Lu presented higher standard deviations (33 %). This is due to the low concentrations of these elements in plants and to their nuclear characteristics, that are not so favourable to activation analysis as the others determined REE.

Table 2. Rare earth elements concentrations in the reference materials "Pine Needles" and "Citrus leaves" by INAA (mg Kg^{-1} dry weight)

Elements	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Pine Needles - NIST 1575								
Obtained data ^a	0.18 ± 0.03	0.36 ± 0.08	0.16 ± 0.03	0.025 ± 0.007	0.0075 ± 0.0007	0.007 ± 0.002	0.013 ± 0.002	0.0015 ± 0.0005
Reference values ^b	0.2	0.4	(0.17)	(0.030)	(0.006)	(0.005)	(0.012)	(0.002)
Citrus Leaves - NIST 1572								
Obtained data ^a	0.16 ± 0.01	0.31 ± 0.03	-	0.060 ± 0.009	0.010 ± 0.001	0.010 ± 0.001	0.024 ± 0.003	-
Reference values ^b	0.19	0.28	(0.16)	(0.052)	(0.009)	(0.010)	(0.027)	(0.004)

^a Mean of 6 determinations

^b Values given by NIST are not certified. Values in parenthesis are data reported by Market & De Li (1991)

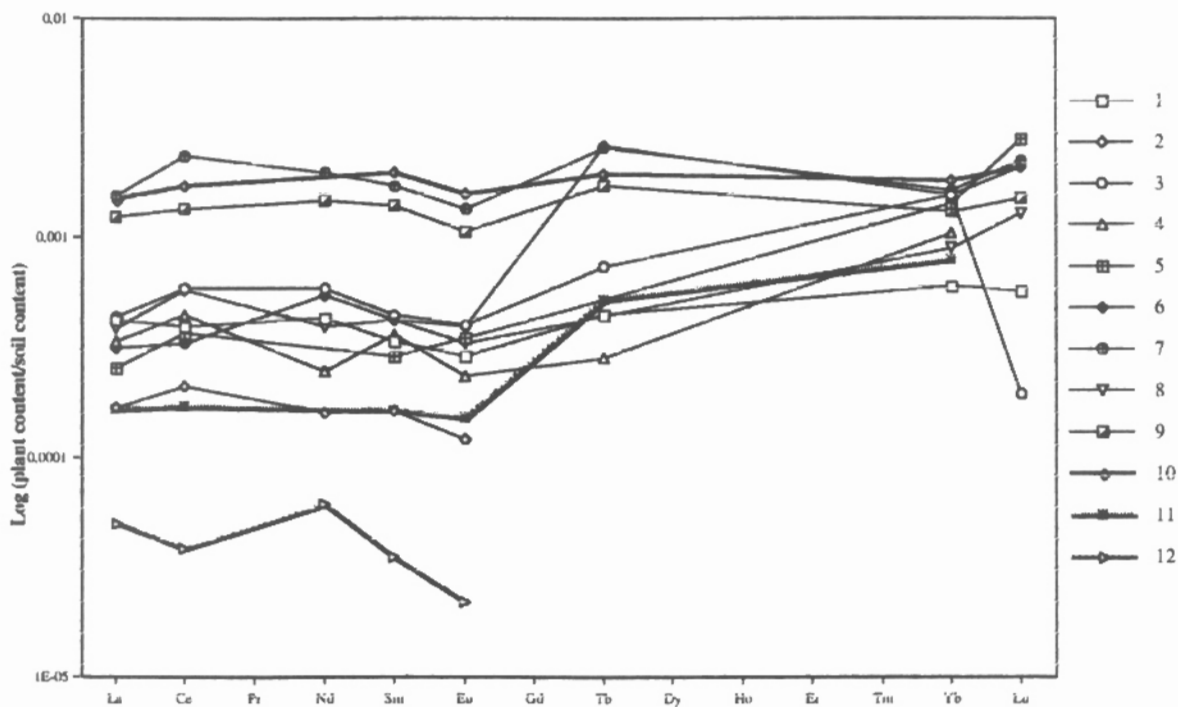


Figure 3. REE contents in various plant species from Lagoa Campestre region normalized to soil content.

Table 3. Rare earth elements^a and Ti^b concentrations in leaves of plants from the region of Lagoa Campestre (mg.Kg⁻¹ dry weight)

Nº	Species	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Ti
1	<i>Dalbergia mischobolium</i>	0.368 ± 0.003	0.629 ± 0.007	0.24 ± 0.03	0.032 ± 0.002	0.0074 ± 0.0002	0.0026 ± 0.0003	0.0050 ± 0.0007	0.0007 ± 0.0002	7.0 ± 0.3
2	<i>Blepharocalyx salicifolia</i>	0.146 ± 0.002	0.337 ± 0.005	0.09 ± 0.01	0.0157 ± 0.0003	0.0031 ± 0.0005	-	-	-	6.0 ± 0.2
3	<i>Lamanonia ternata</i>	0.381 ± 0.007	0.95 ± 0.07	0.33 ± 0.02	0.043 ± 0.002	0.0102 ± 0.0002	0.0043 ± 0.0005	0.0128 ± 0.0005	0.0002 ± 0.0001	32 ± 1
4	<i>Alibertia concolor</i>	0.2935 ± 0.0003	0.718 ± 0.007	0.13 ± 0.02	0.0348 ± 0.0002	0.0060 ± 0.0005	0.0016 ± 0.0002	0.009 ± 0.001	-	15.0 ± 0.3
5	<i>Qualea grandiflora</i>	0.225 ± 0.002	0.59 ± 0.03	-	0.027 ± 0.001	0.0089 ± 0.0003	-	0.0119 ± 0.0007	0.0034 ± 0.0002	20.0 ± 0.8
6	<i>Pteridium aquilinum</i>	0.28 ± 0.02	0.53 ± 0.02	0.30 ± 0.03	0.040 ± 0.002	0.0101 ± 0.0003	0.015 ± 0.003	0.0128 ± 0.0007	0.0025 ± 0.0002	1.00 ± 0.4
7	<i>Diandrostachia chrysotrix</i>	1.36 ± 0.02	3.8 ± 0.1	1.10 ± 0.09	0.17 ± 0.01	0.034 ± 0.001	0.015 ± 0.001	0.014 ± 0.001	0.0027 ± 0.0002	5.0 ± 0.2
8	<i>Gochnatia polymorpha</i>	0.34 ± 0.02	0.93 ± 0.03	0.22 ± 0.03	0.040 ± 0.003	0.0084 ± 0.0003	-	0.007 ± 0.001	0.0015 ± 0.0002	27.0 ± 0.9
9	<i>Erythroxylon sp</i>	1.08 ± 0.02	2.17 ± 0.02	0.81 ± 0.03	0.135 ± 0.003	0.0271 ± 0.0005	0.0099 ± 0.0005	0.0108 ± 0.0003	0.0018 ± 0.0002	1.00 ± 0.04
10	<i>Leandra aurea</i>	1.32 ± 0.02	2.77 ± 0.02	-	0.189 ± 0.009	0.0404 ± 0.0003	0.0114 ± 0.0003	0.0151 ± 0.0005	0.0025 ± 0.0003	4.0 ± 0.2
11	<i>Bauhinia rufa</i>	0.146 ± 0.005	0.27 ± 0.02	-	0.016 ± 0.002	0.0038 ± 0.0002	0.0030 ± 0.0002	0.007 ± 0.001	-	5.0 ± 0.2
12	<i>Stryphnodendron adstringens</i>	0.0441 ± 0.0001	0.061 ± 0.005	0.034 ± 0.002	0.0033 ± 0.0002	0.0006 ± 0.0001	-	-	-	12.0 ± 0.5
	Average content in plants (Markert, 1992)	0.15-0.25	0.25-0.55	0.1-0.25	0.02-0.04	0.005 - 0.015	0.005 - 0.015	0.015 - 0.030	0.0025 - 0.005	3-9.5

^a - INAA; ^b - ICP-AES

In table 3, the values obtained for the concentration of REE in the studied plant leaves are presented (mean of 3 determinations). The average contents in plants (Markert, 1992) are also presented. It can be seen that, for the REE, in general, the values obtained agree with the average contents in plant. Interestingly, the species *Diandrostachia chrysotrix*, *Erythroxyllum sp* and *Leandra aurea* show the highest REE concentrations, specially for the light REE (La to Eu), and the species *Stryphnodendron adstringens* presented the lowest REE contents.

In a study of the content of REE in the species *Solanum lycocarpum* in a similar ecosystem, the alkaline-ultramafic complex of Catalão, GO, Brazil, Lima e Cunha *et al.* (1993) found a very high concentration of REE (600 to 6000 mg Kg⁻¹ in the ashes), much higher than the data obtained in the present work (3 to 200 mg Kg⁻¹).

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 (Markert and De Li, 1991). The obtained factors ranges between 0.0001 and 0.0028, at least ten times lower than the range reported by Markert and De Li (1991) for a natural forest ecosystem (0.041-0.088). This is in agreement with the hypothesis of Markert (1987) that the levels of REE in plants are independent from those of the pedologic substratum; as a result, the high REE level in the soil of the “Lagoa Campestre” area induces low concentration factors for these elements in the plants.

For the comprehension of the diagenesis of REE, the Masuda-Coryell diagram (Masuda, 1962; Coryel *et al.*, 1963) is often used in geochemical studies. It consists in normalizing the REE contents in samples against the REE contents in chondrite meteorite, which is used as a reference (log[REE soil content/REE chondrites content]). The concentration values of REE in the chondrites used are those reported by Boynton (1984). The chondrite-normalized patterns of mean soil value and of the species *Diandrostachia chrysotrix*, *Leandra aurea* and *Erythroxyllum sp*, which present the highest REE contents, are shown in fig. 2 a and b. It can be seen that the studied plants present diagrams very similar to those of the soil, with a high content in light REE (LREE) and a lower one for heavy REE (HREE).

For a better understanding of the relationship between the REE in all studied species and the REE concentrations in the soil, data were also normalized to the mean REE contents in the soils of the area; the obtained diagrams are shown in figure 3. The nearly flat distribution

patterns indicate that, in general, the REE keep in the plants the same distribution as the one found in the soil.

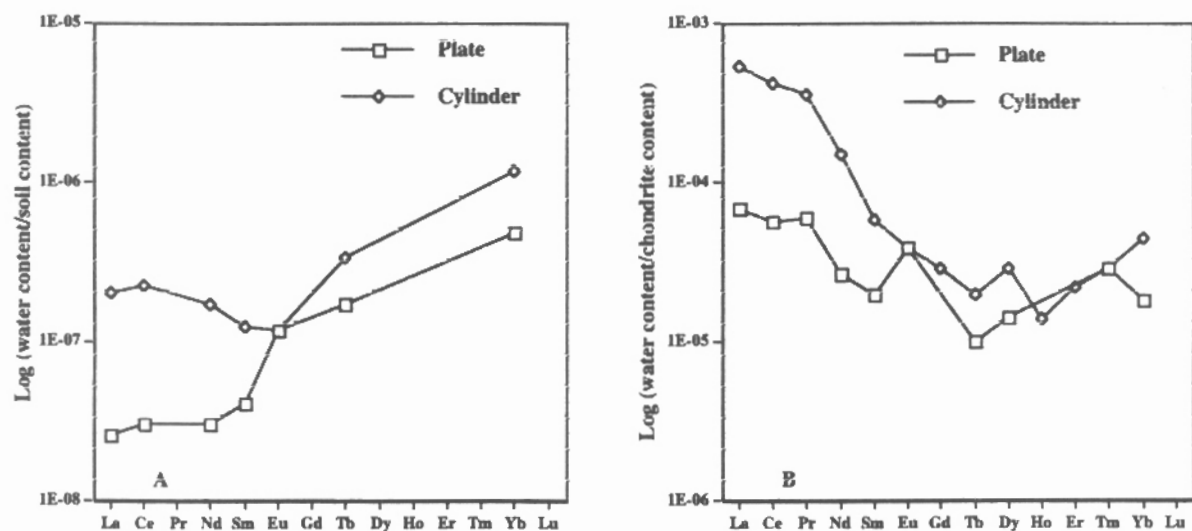


Figure 4. REE contents in groundwater from Lagoa Campestre region normalized to soil (A) and chondrites (B) content.

Table 4. Rare earth elements concentrations in surface waters collected in the lysimeter (10 cm depth), by ICP-MS ($\mu\text{g L}^{-1}$)

Collector Type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Plate	0.023	0.049	0.007	0.017	0.004	0.003	-	0.001	0.005	-	0.001	0.001	0.004	-
Cylinder	0.18	0.366	0.042	0.096	0.012	0.003	0.008	0.002	0.010	0.001	0.005	0.001	0.01	-

The results obtained for the REE concentrations in groundwaters sampled in the two different types of collectors are shown in table 4. For this study, only the waters collected in the superficial horizon (10 cm depth) are considered because the roots are mainly active at this level in the studied area. The sum of REE ranges from 0.2 to $0.08 \mu\text{g L}^{-1}$. The distribution patterns of the REE in superficial water normalized both to the soils and to the chondrites content are shown in figure 4 a and b respectively. The soil-normalized pattern is different from that observed for the plants and the soils; it indicates an enrichment in HREE in the waters with respect to mean soil value. This tendency is mainly evident in the water collected in the plate-type collector, which is much more affected by the root activity. The chondrite-normalized pattern for his part is more or less similar to those obtained for the soil and plants.

The species *Lamanonia ternata*, *Qualea grandiflora* and *Gochnatia polymorpha* present Ti concentrations much higher than the reference values (table 3). Actually, *Qualea* as well as other Vochysiaceae, are already known as aluminium accumulator (Kukachka & Miller,

1980). Ti is one of the so called "high field strength elements" (Hall & Plant, 1992), usually presenting a weak mobilization by weathering processes. Therefore, a high Ti accumulation was not expected in the plants, even with the high Ti soil content.

CONCLUSIONS

Despite the high levels of REE found in the soils, plants growing in the alkaline-ultramafic complex of Salitre, in a tropical environment, generally present REE concentrations within the ranges usually found in plants. The highest REE contents are found in species *Diandrostachia chrysotrix*, *Leandra aurea* and *Erytroxylum sp.* However for every species, the transfer factor from soil to plant is at least ten times below the range reported in the literature, confirming that the concentration of REE in the plants are widely independent of the soil content. All species present normalized patterns similar to those of the soils, characterized by an enrichment in LREE. One should also notice that in the studied area, *Lamanonia ternata*, *Qualea grandiflora* and *Gochnatia polymorpha* present Ti concentrations about tree times higher than the reference values.

Our results suggest also that in the studied ecosystem the metabolism of plants affect the REE distribution in the groundwaters, leading to an enrichment of the surficial waters in HREE.

ACKNOWLEDGMENTS

The authors wish to thank B. Dupré for support in waters analysis, M. Meguro for the use of her laboratory to prepare plant analysis, P. Magat and H. L. Ozorio F. for field assistance. This work was supported by French ECOFIT Program (ORSTOM-CNRS) and, in Brazil, by FAPESP: Projeto Tematico, processo 91/3518-0.

REFERENCES

- BOYTON W.V. Cosmochemistry of the rare earth elements: meteorite studies. In: P. Henderson (ed): *Rare earth element geochemistry*. Elsevier, 63-114.
- BROOKS R.R., 1972. *Geobotany and biogeochemistry in mineral exploration*. Harper & Row Publishers.
- CAPLAN J., LOBERSLI, E., NAEUMANN R., STEINNES E., 1987. A neutron activation study of trace element contents in plants growing on soils of different acidity. *J. Radioanal. Nucl. Chem.*, Articles, 114, 13-19.
- CHAUVEL, A., ANDREUX, F., CERRI, C.C., LUCAS, Y., 1989. Superficial evolution of amazonian bauxite deposits. *Trav. ICSOBA, Acad. Youg. Sci. Arts*, 19: 45-53.

- HALL G.E.M., PLANT, J.A., 1992. Application of geochemical discrimination diagrams for the tectonic interpretation of igneous rock hosting gold mineralization in the Canadian Shield. *Chem. Geol.*, 95, 157-165.
- ICHIASHI H., MORITA H., TATSUKAWA R. 1992. Rare earth elements (REEs) in naturally grown plants in relation to their variations in soils. *Environmental Pollution*, 76, 157-162.
- LIMA E CUNHA M.C., FORMOSO M.L., PEREIRA V.P., 1993. Estudos biogeoquímicos no complexo alcalino-ultramáfico de Catalão I, Goiás. *Extended abstracts of the VI Congresso Brasileiro de Geoquímica*, SBGq, 1993, p. 268-289.
- KUKACHKA B.F., MILLER R.B., 1980. A chemical spot-test for aluminium and its value in wood identification. *IWA Bull.* n.s. 1, 104-109
- MARKERT B., PIEHLER H., LIETH, H., SUGIMAE A., 1989. Normalization and calculation of lanthanide element concentration in environmental samples. *Radiat. Environ. Biophys.*, 28, 213-221.
- MARKERT B., 1992. Presence and significance of naturally occurring chemical elements of the periodic system in the plant organism and consequences for future investigation in organic environmental chemistry in ecosystems. *Vegetatio*, 103, 27-35.
- MARKERT B., DE LI Z., 1991. Natural background concentrations of rare-earth elements in a forest ecosystem. *The Science of the Total Environment*, 103, 27-35.
- MARKERT B., 1987. The pattern of distribution of lanthanide elements in soils and plants. *Phytochemistry*, 26, 3167-3170.
- SONDAG F., SOUBIES F., FORTUNE J.P., DUPRE B, MAGAT P., MELFI A., 1997. Hydrogeochemistry in soils of the "Lagoa Campestre" basin (Salitre, MG, Brazil): dynamics of rare earth elements., *Appl. Geochem. Suppl. Issue*, 11:1-9.
- ULBRICH H.H., GOMES C.B. 1981. Alkaline rocks from continental Brazil. *Earth Sci. Rev.*, 17, 135-154.
- YLIRUOKANEN I., 1975. A chemical study on the occurrence of rare earths in plants. *Ann. Acad. Sci. Fenn.*, ser. Az, 176, 1-28.