Biogeochemistry of Trace Elements (Ti, REE, ...) under "cerrado" cover in Central Brazil ("Lagoa Campestre", Salitre, MG)

Ceccantini, G. (1), Figueiredo, A. M. G. (2), Sondag, F.(3), Soubiès, F.(3) (4)

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(1) Instituto de Biociências, University of São Paulo (USP), Brazil
(2) Instituto de Pesquisas Energeticas e Nucleares (IPEN), São Paulo, Brazil
(3) Laboratoire des Formations Superficielles - UR 12, TOA Dept. ORSTOM, Bondy, France
(4) Laboratoire de Minéralogie, UPS, Toulouse, France

Abstract

The "cerrado" is a savanna-like formation of Central Brazil characterized essentially by the tortuosity of the trees and the leaf stiffness. The role of this vegetation on the secondary dispersion of some trace elements was investigated in a tropical area where carbonatitic complexes, rich in Ti, Rare Earth elements (REE), Zr, Nb, ..., occurs and plant samples analysis was combined with surface water analysis.
The REE absolute content of vegetal ashes is high, as might be expected due to the high levels observed in the soils, but falls within the usual range found by other workers and no relation between the plant habit (tree, shrub, herb) and the REE content is found. A weak fractionation occurs for some species: it concerns Ce and HREE and is similar to that observed in the surface waters collected in a plate lysimeter where roots are active.The high Ti content in some species may indicate that these species are Ti accumulators .

Introduction

The "cerrado" is a savanna-like formation that covers wide areas in Central Brazil (~ 1.5 x 10^6 km^2). The most conspicuous features of this vegetation is the tortuosity of the trees and the leaf stiffness. The fires are very frequent but the plants are well adapted against it : barks are very thick, roots are deep and there exist many kinds of underground organs for carbohydrates and water storage (Rizzini, 1979). The role of this vegetation on the secondary dispersion of some trace elements was investigated in a area where carbonatitic complexes occur.

Environment

Several ultramafic-alkaline complexes occur in the Alto Paranaiba area, in the West of Minas Gerais State (ULBRICH and GOMEZ, 1981). One of these, the Salitre complex, comprising mainly micaceous pyroxenites ("bebedourite") or peridotites and some carbonatites, has a central, dolina-shaped, depression ("Lagoa Campestre") partially filled by sediments and occupied by a peaty lake (Fig. 1). A thick, loose latosolic cover (hematite, gœthite, gibbsite, kaolinite, quartz, anatase, crandallite family phosphates) surrounds the depression, overlying a thick saprolite (50-100 m). Due to the particular mineralogy of the bedrock, where perovskite, apatite and calzirtite are often essential minerals, these alterites have high contents in TiO_2 (up to 30%), REE (up to 5% ΣR_2O_3), ZrO_2 (up to 1%) and Nb_2O_5 (up to 1%).
The climate is tropical, characterized by a mean annual temperature of ± 20°C and a rainfall of ± 1500 mm; the length of the dry season reaches five months, from July to November. The original vegetation consists of semideciduous forest and arboreal savanna ("cerradão") but nowadays the cover is a mosaic of largely modified physionomy of cerrado (human activity : coffee and ranch).
The sampled area (plants, soils and waters) is situated at the border of the Lagoa Campestre, in a zone of secondary cerrado cover (Fig. 1).

Material and methods

Plants

Plant samples were collected from the cerrado area at the neighborings of a lysimeter (see below) during the the dry season (August 1993). The 14 most frequent species (7 trees, 5 shrubs, 2 herbs - each class with variable root deep) were choosen in a broad variation of tropical plant families (1 fern,

12 angiosperm families). Fresh leaves and other organs (stem/wood and root not yet analysed) were collected (300-500 g) to obtain at least 50-100 g when dry. Each sample was washed many times using abundant deionized water, dryed, and homogenized with a mixer. The powder was put into ceramic capsules, dryed at 105 °C for 24 h, weighted and ashed in a electric oven at 450 °C for 12 h. The ashes were divided and each plant sample was analysed by INAA and ICP-AES.
For the analysis by INAA, each ash sample or standard were sealed in a polyethylen bag and irradiated during 8 hours in $10^{12} n.cm^{-2}.s^{-1}$ termic neutron flow, in the IEA-R1 reactor of IPEN-São Paulo. The countings of induced gama radiation were made by a high purity Ge detector, with resolution of 1,90 keV for the 1332 keV ^{60}Co peak, conected to a ACE 8K ORTEC plate. For analysis of the obtained spectra was employed the VISPECT software developed in the Radiochemistry Supervision. Two series (2-4 h) of measures were taken 5 and 20 days after the irradiation. The reference materials used were "Citrus Leaves", "Pine Needles" (NIST) and "BE-N" (ANRT).

Water and soil

Water samples were collected during and at the end of the dry season (June 93 and November 93 respectively) and at the end of the rain season (March 94). A pan-type lysimetric experiment was installed under weakly disturbed cerrado. It consists of i) cylindrical lysimeters containing undisturbed soil samples and ii) collectors in form of plates settled in a pit at 10, 25, 45 and 85 cm depth. On the one hand, the cylindrical lysimeters are isolated from the surrounding soil; so, they are not penetrated by roots and the collected leachates represent 80 to 95 % of the rainwater drained vertically. On the other hand, the plate collectors do not prevent the root penetration and their adsorption activity, and they collect only rapid circulating water representing 2 to 10 % of rainwater (Sondag et al, 1995).
The samples were immediately filtered (0,2 µm) and a subsample was acidified for traces and REE 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 the vicinity of the lysimetric experiment. Major elements were determined by ICP-AES after melting with $LiBO_2$ and dilution in 2N HNO_3; trace elements, including REE, were also determined using ICP-AES after a mixed $HClO_4$ - HF digestion.

Results

Rare Earth Elements

REE values in the different plant samples are listed at Table I. The REE absolute content of vegetal ashes is high, as might be expected due to the high levels observed in the soils, but falls within the usual range found by other workers (Yliruokanen, 1975, Ichiashi et al., 1992). *Diandrostachia chrysotrix* has the highest REE content. This specie is a grass, about 60 cm high, with a well developped root system that extends within a radius of about 1 m and till 50 cm depth. It is one of the dominants in the herbaceous stratum in the cerrado areas around the Lagoa Campestre, thus its role may be very important in the cycling of REE. Its biomass is not yet estimated.
No relation between the plant habit (tree, shrub, herb) and the REE content is found (Fig. 2). This result desagrees with those found by Ichiashi et al. (1992).
Owing to the great homogeneity of REE values in the different soil horizons of the lysimeter (Table II), REE contents of the plants and of the waters collected in the lysimeters were normalised to the average value of these soil samples (Fig. 3). For this study, only the superficial waters are of concern because of the high density of roots and mycorhizes in the surface horizon.
For the waters, the sum of REE concentrations ranges from 0.2 to 0.8 ppb; the REE abundance normalised to average REE value of the surrounding soils shows an enrichment in HREE (Fig. 3).
In the plants, a weak fractionation occurs for some species: it concerns Ce and HREE and is similar to that observed in the surface waters collected in the plate lysimeter where roots are active.

Titanium

The high Ti content in *Alibertia concolor*, *Gochnatia polymorpha*, *Lamanonia ternata*, and *Qualea grandiflora* may indicate that these species are Ti accumulators (see Ti content in dry leaves at Table III). In fact the genus *Qualea* , as well the other Vochysiaceae, are known as aluminium accumulators. An anatomic study of these species is being conducted in such a way to understand some aspects of the physiology of metal accumulations in plant tissues.

Scleromorphism index

The scleromorphism index is a variable that measures the leaf stiffness, usualy applied for comparing the level of xerophytism among ecosystems. It is calculated with the formula:

leaf dry weight/2 x leaf area.

We determine this index (average of 25 leaves) for 10 species (Table III).
Usualy, this index is high for dry and poor in nutrients formations (cerrado, savanna) and low for wet and richer vegetations (rain forests, semideciduous forests). For the moment, we only found references about relation between the scleromorphysm index and the main nutrients in the soil (N, P, K) (Rizzini, 1976) but none about the trace elements in the plants. Therefore, we investigate the possible correlation of this index with the trace elements content of the cerrado plants. We found that only a weak correlation appears between the scleromorphism index and the values of Cs ($r = 0.8$, $N = 6$). The meaning of this correlation remains unexplained. Its confirmation requires the analysis of more samples.

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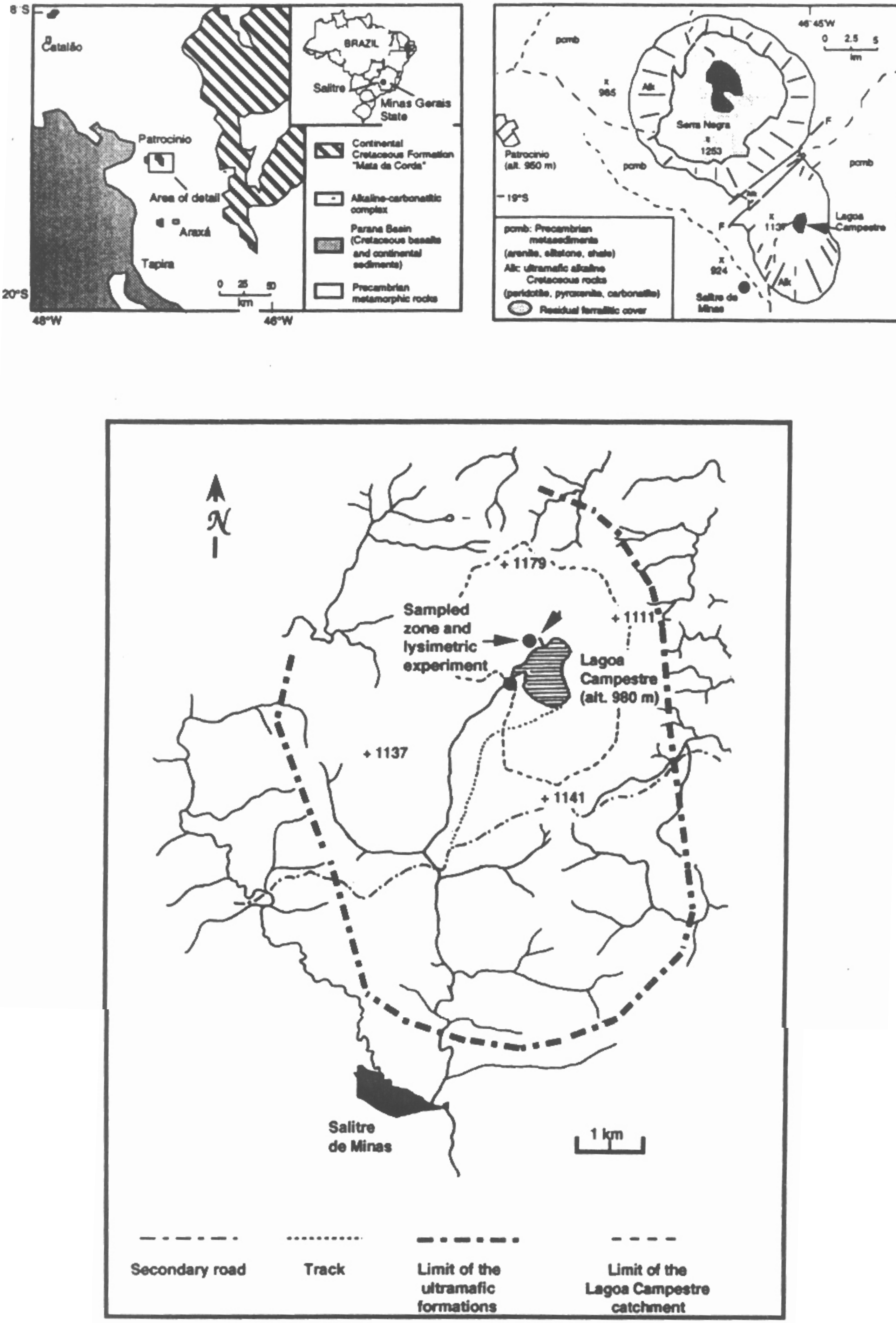
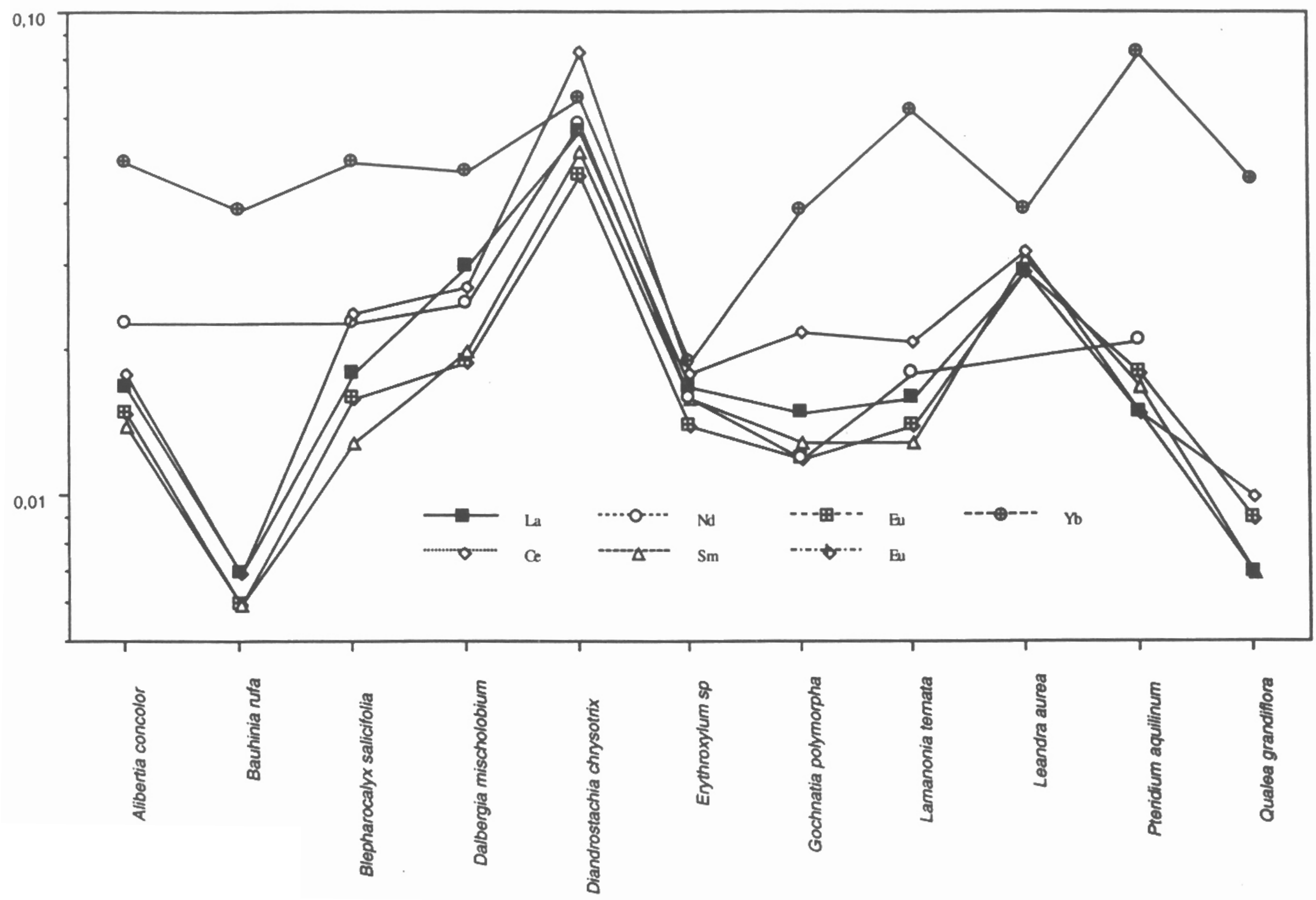
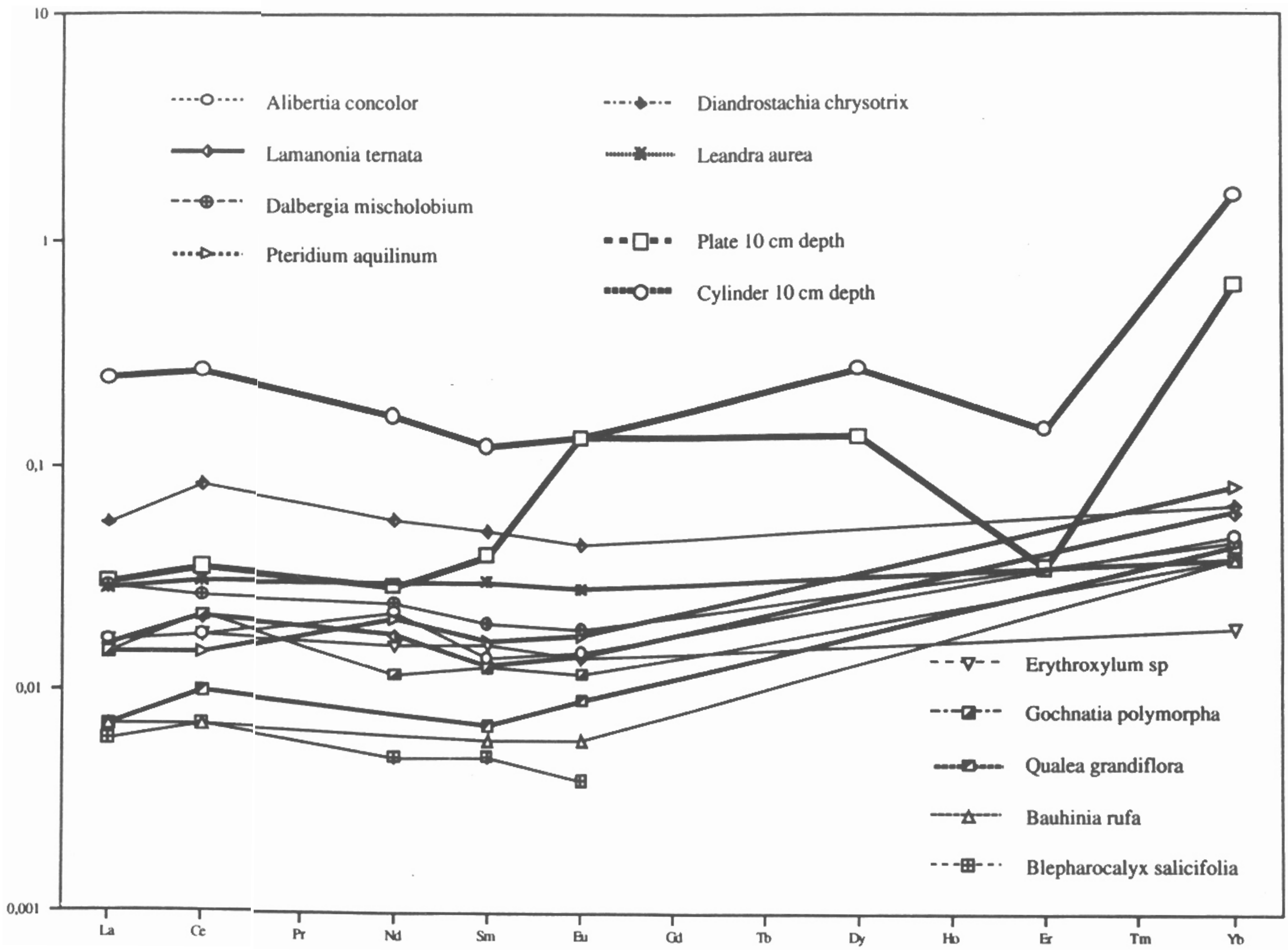
Figure 1: Localisation of the Salitre area, geological context, drainage system and location of sampled zone and of the lysimetric experiment. (+ 1137 = altitude in meters)

Figure 2 : REE abundance in the different plant species (values normalised to the mean REE abundance in soil samples).

Figure 3 : REE abundance in plant and water samples (values normalised to the mean REE abundance in soil samples).


8°S
Catalão
BRAZIL
Salitre
Minas Gerais State
Patrocinio
Area of detail
Araxá
Tapira
20°S
48°W
46°W
0 25 50
km
Continental Cretaceous Formation "Mata da Corda"
Alkaline-carbonatitic complex
Parana Basin (Cretaceous basalts and continental sediments)
Precambrian metamorphic rocks
pcmb
46°45'W
0 2.5 5
km
x 985
Alk
Serra Negra
x 1253
F
Patrocinio (alt. 950 m)
19°S
x 1137
Lagoa Campestre
x 924
Salitre de Minas
pcmb: Precambrian metasediments (arenite, siltstone, shale)
Alk: ultramafic alkaline Cretaceous rocks (peridotite, pyroxenite, carbonatite)
Residual ferralitic cover
N
+ 1179
+ 1111
Sampled zone and lysimetric experiment
Lagoa Campestre (alt. 980 m)
+ 1137
+ 1141
Salitre de Minas
1 km
Secondary road
Track
Limit of the ultramafic formations
Limit of the Lagoa Campestre catchment


0,10
0,01
La
Ce
Nd
Sm
Eu
Eu
Yb
Alibertia concolor
Bauhinia rufa
Blepharocalyx salicifolia
Dalbergia mischolobium
Diandrostachia chrysotrix
Erythroxylum sp
Gochnatia polymorpha
Lamanonia temata
Leandra aurea
Pteridium aquilinum
Qualea grandiflora


10
1
0,1
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La
Ce
Pr
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Tb
Dy
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Tm
Yb
Alibertia concolor
Lamanonia ternata
Dalbergia mischolobium
Pteridium aquilinum
Diandrostachia chrysotrix
Leandra aurea
Plate 10 cm depth
Cylinder 10 cm depth
Erythroxylum sp
Gochnatia polymorpha
Qualea grandiflora
Bauhinia rufa
Blepharocalyx salicifolia

Table I: REE content (ppm) in leaf ashes of plants from the cerrado formation around the lysimeter.

Species	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Alibertia concolor	12,0	25,00	13,00	1,40	0,34	0,18	0,30	0,05
Bauhinia rufa	5,3	10,00		0,57	0,14	0,11	0,24	
Blepharocalyx salicifolia	13,0	33,00	13,00	1,30	0,35	0,12	0,30	0,06
Dalbergia mischolobium	21,5	36,70	14,00	1,90	0,43	0,15	0,29	0,04
Diandrostachia chrysotrix	41,0	115,00	33,00	5,00	1,03	0,45	0,41	0,08
Erythroxylum sp	12,0	24,00	9,00	1,50	0,30	0,11	0,12	0,02
Gochnatia polymorpha	11,0	30,00	7,00	1,30	0,27		0,24	0,05
Lamanonia ternata	11,6	29,00	10,00	1,30	0,31	0,13	0,39	0,01
Leandra aurea	21,0	44,00		3,00	0,64	0,18	0,24	0,04
Pteridium aquilinum	11,0	21,00	12,00	1,60	0,40	0,60	0,51	0,10
Qualea grandiflora	5,3	14,00		0,65	0,21		0,28	0,08

Table II : REE content (ppm) in the different horizons (depth in cm) of the lysimetric profile and in the surrounding soils (mean value)

	La	Ce	Nd	Sm	Eu	Dy	Er	Yb
0-10	653	1204	487	85	19	28	26	5
10-25	677	1260	516	89	20	30	27	5
25-45	715	1319	550	93	22	31	28	5
45-85	729	1352	551	96	22	34	29	5
85-120	727	1329	545	88	21	32	33	5
Mean of surrounding soils (N = 20)	725	1370	563	97	22	36	33	6

Table III : Major and trace elements content in leaf ashes of plants from the cerrado formation around the lysimeter and scleromorphism index (SI).

Species	Na	K	Rb	Cs	Mg	Ca	Sr	Ba	Sc	Ti	Zn	Co	P	Th	U	Ash	Ti	SI
	%	%	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	% dm	ppm dry mat.	
Alibertia concolor	0.12	12.20	217	15.0	4.65	13.57	2591	4919	2.5	278	192	1.6	11.30	2.5		5.44	15	0.98
Bauhinia rufa	0.08	3.52			1.78	10.23	624	6122		94	569		7.48			5.44	5	0.79
Blepharocalyx salicifolia	0.20	17.87	214	18.0	4.78	10.10	1955	153	2.3	666		3.4	3.78	2.3	0.64	0.97	6	1.03
Dalbergia mischolobium	0.21	14.87	451	28.0	7.61	18.30	5186	1671	2.3	668	631	7.8	5.42	2.4	0.32	1.03	7	1.03
Diandrostachia chrysotrix	0.26	6.64	286	41.0	1.51	3.12	221	930	4.4	138	230	6.7	4.28	7.4	1.30	3.33	5	
Erythroxylum sp	0.09	2.06	72	12.0	1.63	4.74	137	1918	1.5	46	109	1.6	4.40	2.3	0.32	1.21	1	
Gochnatia polymorpha	0.23	18.44	540	13.4	4.52	9.20	466	2337	1.6	876	980	2.2	3.20	2.1	0.40	3.09	27	1.21
G. polymorpha - stem	0.17	21.90			4.73	7.42	1124	2734		1310			4.79					
Lamanonia ternata	0.23	15.92	251	6.0	6.45	17.38	4211	2101	2.6	971		114.0	8.32	2.7	1.30	3.28	32	0.64
Leandra aurea	0.05	4.47			2.40	10.82	1583	4593		75			2.28			5.44	4	
Pteridium aquilinum	0.14	5.82	761	0.4	2.22	4.33	245	1487	1.3	44	199	2.3	3.76	1.6	0.37	2.52	1	
Qualea grandiflora	0.13	11.34	274	33.0	1.96	7.14	3211	997	0.5	469		1.4	6.04	1.4	0.48	4.23	20	1.03
Rapanea cf lancifolia	0.24	25.64			6.52	12.66	1394	470		433			2.95			3.28	14	0.74
Stryphnodendron sp	0.18	22.95			7.93	9.81	908	334		376			6.69			3.23	12	0.70
Zanthoxylum obscurum	0.13	22.32			5.65	9.64	2524	154		292			8.13			6.67	19	0.97