



## Biogeochemistry of REE elements and tetrad effect in the soil-plant system: a study on volcanic rock covers in southernmost Brazil

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### ABSTRACT

This paper deals with the distribution of REE in rock, soil and plant in an area of monzonitic rocks from southernmost Brazil. The REE patterns in *Schinus lentiscifolius* show a negative-Ce anomaly and a prominent tetrad effect, characterized as W-type that are not present in rock and soil samples. The REE patterns in the soils and rocks sampled are very similar and there is no fractionation of REE during the processes of soil formation. The W-type patterns are interpreted as indicating that REE were absorbed by *S. lentiscifolius* as simple ions rather than as complex ions, or, alternatively, that the transport of REE in the plant metabolic processes was as free ions. The recognition of tetrads, either, M- or W-type patterns, is an additional tool for understanding the biogeochemistry of REE and can contribute to the study of monitoring processes of contaminated environment or to mineral prospecting.

**Key words:** REE, tetrad effect, *Schinus lentiscifolius*, southernmost Brazil.

### INTRODUCTION

The rare earth elements - REE - are concentrated mainly in accessory minerals of igneous or metamorphic rocks, and show low mobility in these high-temperature systems (Henderson 1984). Hydrothermal and weathering fluids, however, can mobilize the REE mainly by forming soluble complex ions (Nesbitt 1979, Topp et al. 1984, Lottermoser 1990). The concentration of REE in soils depends on the composition of source rocks, the weathering conditions, the organic matter content, among other factors, but in general the light REE (LREE) predominate over the heavy ones in the shallower layers, HREE (Tyler 2004). Plants under

natural conditions absorb minimal amounts of REE (1 to 45 ppm -wt% in ash) (Kabata-Pendias and Pendias 1984), although some species are capable of accumulating high levels of REE contents, in spite of their low solubility of REE in soil solutions (Milton et al. 1944, Evans 1990, Osaki and Enomoto 2001, Tyler 2004). The REE are more soluble as chlorides, nitrates and perchlorates than in the form of carbonates, hydroxides and fluorides (Evans 1990). According to McLennan (1994) the chemical behavior of REE is controlled by their ionic radii, charge, volatility and stability of their complexes. A fifth factor named tetrad or double-double (Masuda and Ikeuchi 1979) is described by McLennan (1994) as "a marked increase in stability represented by the half (Gd) and completely filled (Lu) 4f electron shell

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and lesser but still significant increases in stability associated with the quarter (between Nd and Pm) and three-quarter filled (between Ho and Er) 4f shell". McLennan (1994) considered that the tetrad effect is most apparent in natural waters or rocks that have interacted with fluids. Accordingly, sea water and material precipitated directly from sea water would possess "W-type" effects with four concave up segments to the REE pattern. Other materials displaying the tetrad effect due to interaction with water would possess "M-type" effects with four convex up segments in the REE pattern. Following Sastri et al. (2003), it is concluded that the tetrad effect reflects discontinuities in the third ionization potential of REE. Such discontinuities are also shown in the energy involved in the formation of complexes, so that, Nd-Pm, Gd, Ho-Er, and Lu demand more energy for forming complexes than their neighbors. That is the reason why they are depleted in relation to their neighbors (i.e. M-type pattern) in solutions where they are kept as complexes.

Fractionation of REE, including tetrad effects, has been reported by several authors (Fu et al. 1998, Wyttenbach et al. 1998, Ding et al. 2006, Ding et al. 2007, Lima e Cunha et al. 2010). However, mechanisms and controls of REE distribution and translocations in these systems, and in the vegetal structures are still poorly known. Further studies are needed, since the slight modifications in the REE capable of generating tetrad effects can affect their accumulation in plants, water and soils.

In this paper we discuss the distribution of REE in rock, soil and plant in an area of monzonitic rocks with copper-Au-sulphide mineralizations in order to contribute to the comprehension of REE geochemistry in the soil-plant system.

#### MATERIALS AND METHODS

The study area is situated nearby the city of Lavras do Sul, southernmost Brazil. The vegetation of the area consists of scrub forest in association with

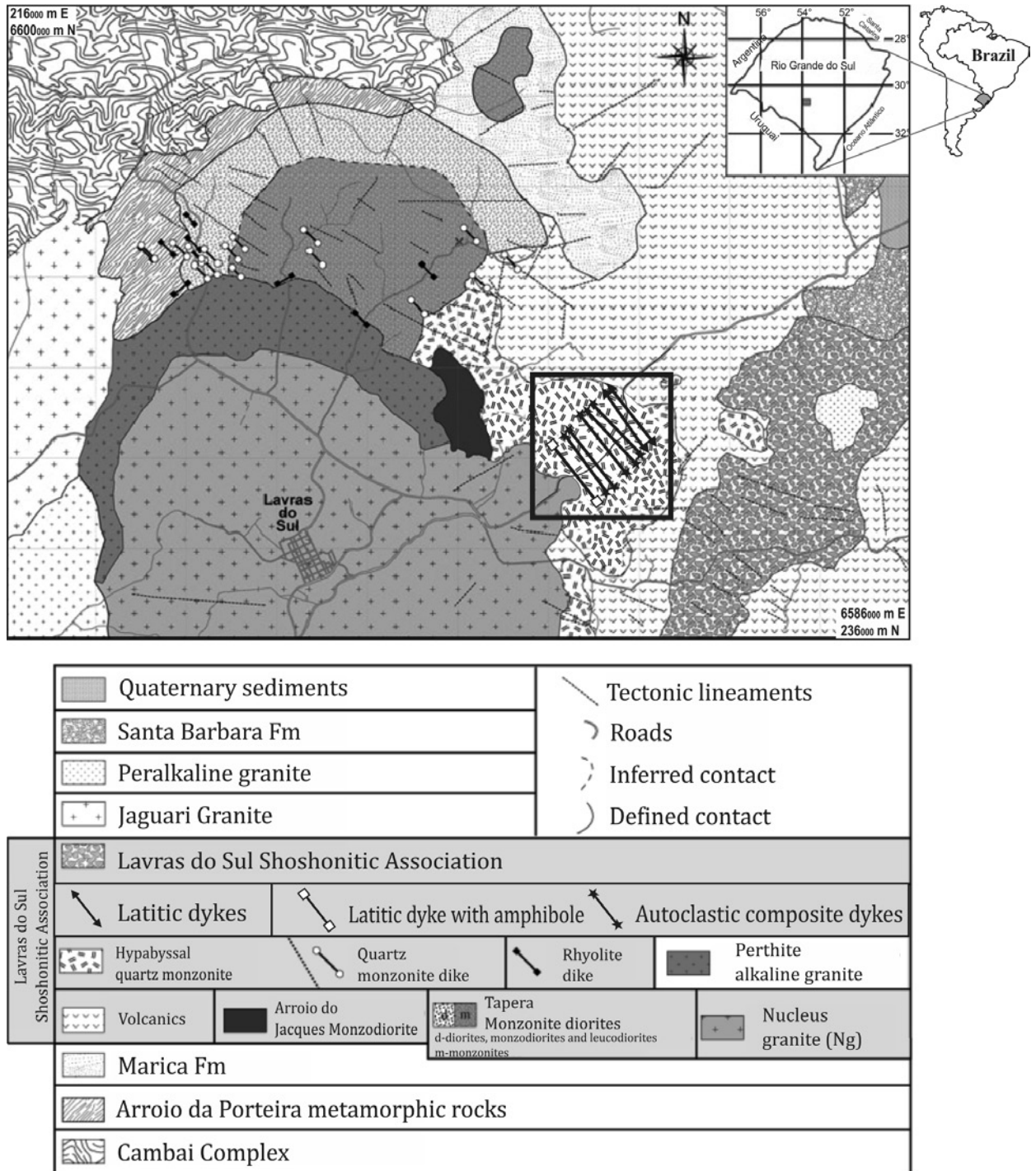
grass fields and thin lithosoils. The plant species selected for sampling, *Schinus lentiscifolius* (mastic), is a shrub about 2 or 3m high with wide area distribution, easy recognition and high density, which simplifies the collection. The region of Lavras do Sul is dominated by volcanic and plutonic rocks which belong to the Lavras do Sul Shoshonitic Association (Nardi and Lima 1985), and the predominant lithologies in the study area are monzonites, quartz monzonites, rhyolites and latite dikes, (Liz et al. 2009).

Plant (10) and soil (5) samples were collected in places where some of these rocks have Cu-Au-sulphide mineralization (Fig. 1). In pre-processing, the selected organ (leaf) were washed with distilled water, dried at 80°C and calcined (450°-500°C) for a period of 6 to 8 hours (Brooks 1983), and the determination of the REE (in ash) was carried out by ICP-MS. The detection limits (in ppm) are 0.002 for La, Pr, Nd; 0.01 for Ce; 0.001 for Sm, Eu, 0.01 for Gd, and 0.001 for Tb, Dy, Ho, Er, Tm, Yb and Lu. The soil samples were dried, quartered and sieved and the fraction less than 200 mesh was separated by decanting. The resulting material (0.5 g) was subjected to fusion with a mixture of lithium metaborate - lithium tetraborate and analyzed by ICP - MS. The limits of detection for REE are the following: 0.05 for La, Ce and Nd; 0.01 for Pr, Sm, Gd, Tb, Dy, Ho, Er and Yb, 0.005 for Tm and Eu, 0.02 for Lu.

The analytical procedures for all samples were performed by Act Labs, Canada. The REE patterns in figures 2a, 2b and 2c, were calculated based on C1 chondritic values after Evensen et al. (1978).

#### RESULTS

The REE chondrite-normalized patterns are broadly similar in rock (Fig. 2c), soil (Fig. 2b) and plant samples (Fig. 2a), although the contents in plant samples are about ten times lower than in soils and rocks. The contents of REE and some of their representative parameters in soils, rocks and plants are in Tables I and II, respectively.



**Figure 1** - Geological map with outline of the area modified from Liz et al. (2009). The square highlights the area where samples were collected along the road. The letters represent the lithologies of the Lavras do Sul Shoshonitic Association - ASLS. Maj - Arroio dos Jaques Monzonite; Mh - Hypabyssal Monzonites, V - Volcanic rocks; Ng - Lavras do Sul Granite Cv - Volcanic Conglomerate.

**TABLE I**  
REE concentrations in ash leaves of *Schinus lentiscifolius*. Values in ppm.

| Sample | DK 01 | DK 02 | DK 03 | DK 04 | DK 05 | DK 06 | DK 07 | DK 08 | DK 09 | DK 10 |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| La     | 12.2  | 13.8  | 6.32  | 8.72  | 4.58  | 2.83  | 2.34  | 2.74  | 5.22  | 4.26  |
| Ce     | 7.09  | 11.5  | 4.7   | 6.99  | 4.5   | 2.19  | 1.25  | 1.34  | 2.68  | 1.84  |
| Pr     | 1.44  | 2.45  | 0.928 | 1.93  | 0.56  | 0.411 | 0.233 | 0.256 | 0.512 | 0.522 |
| Nd     | 4.76  | 8.75  | 3.19  | 8.04  | 1.99  | 1.49  | 0.756 | 0.826 | 1.55  | 1.81  |
| Sm     | 0.722 | 1.32  | 0.518 | 1.32  | 0.285 | 0.207 | 0.101 | 0.105 | 0.192 | 0.225 |
| Eu     | 0.056 | 0.191 | 0.11  | 0.289 | 0.076 | 0.047 | 0.041 | 0.047 | 0.055 | 0.053 |
| Gd     | 0.69  | 1.33  | 0.56  | 1.3   | 0.29  | 0.2   | 0.1   | 0.11  | 0.2   | 0.22  |
| Tb     | 0.063 | 0.133 | 0.057 | 0.134 | 0.027 | 0.019 | 0.01  | 0.01  | 0.016 | 0.019 |
| Dy     | 0.212 | 0.521 | 0.232 | 0.556 | 0.094 | 0.076 | 0.038 | 0.037 | 0.057 | 0.065 |
| Ho     | 0.034 | 0.09  | 0.043 | 0.102 | 0.016 | 0.013 | 0.007 | 0.007 | 0.01  | 0.013 |
| Er     | 0.082 | 0.222 | 0.106 | 0.265 | 0.045 | 0.036 | 0.02  | 0.018 | 0.028 | 0.032 |
| Tm     | 0.007 | 0.021 | 0.011 | 0.025 | 0.005 | 0.004 | 0.003 | 0.003 | 0.003 | 0.003 |
| Yb     | 0.04  | 0.102 | 0.059 | 0.124 | 0.036 | 0.022 | 0.023 | 0.024 | 0.02  | 0.022 |
| Lu     | 0.007 | 0.015 | 0.01  | 0.019 | 0.009 | 0.004 | 0.006 | 0.006 | 0.005 | 0.005 |

**TABLE II**  
Average contents of REE in plant (*Schinus lentiscifolius*), soil and rock samples.

| Plant                 | Soil  | Rock   |
|-----------------------|-------|--------|
| $\Sigma$ REE          | 16.46 | 237.39 |
| $\Sigma$ LREE (La-Eu) | 15.54 | 221.20 |
| $\Sigma$ HREE (Gd-Lu) | 0.92  | 16.19  |
| LREE/HREE             | 20.69 | 13.66  |
| LaN/YbN               | 90.10 | 21.24  |
|                       |       | 26.34  |

REE patterns in plants show negative-Ce anomalies that are not present in rock and soil samples. The intensity of Ce anomalies is represented by: the Ce content determined, divided by the Ce estimated (Ce\*) from the average of their neighbors (La and Pr), considering the normalized values. In the plant samples the Ce/Ce\* ratio varies from 0.25 to 0.58, indicating clear negative anomalies in all samples.

The other important feature that is recognized only in plant patterns is the prominent tetrad effect characterized as W-type due to the concave-up pattern segments (Fig. 2a). The intensity of the tetrad effect was measured in the graphics, as suggested by Irber (1999): values of T1 (La-Ce-Pr-Nd), T3 (Gd-Tr-Dy-Ho) and T4 (Er-Tm-Yb-Lu) significantly larger than 1 indicates that the M-type pattern

occurs, while values significantly lower than 1 indicate the W-type effect. T2 value is difficult to be calculated because of Eu variable behavior. T1, T3, and T4 values for plant samples in the studied area are respectively 0.87, 0.82, 0.80; and the T1,3 value, which represents the average of T1 and T3 is 0.84.

REE patterns in the soils and rocks sampled are very similar (Fig. 2b and 2c), and, there is no fractionation of REE during the processes of soil formation. These patterns are typical of rocks of shoshonitic affinity as described previously by Lima and Nardi (1998) and Liz et al. (2009).

## DISCUSSION

The REE patterns of the *Schinus lentiscifolius* show clear differences from those of soils and rocks in the

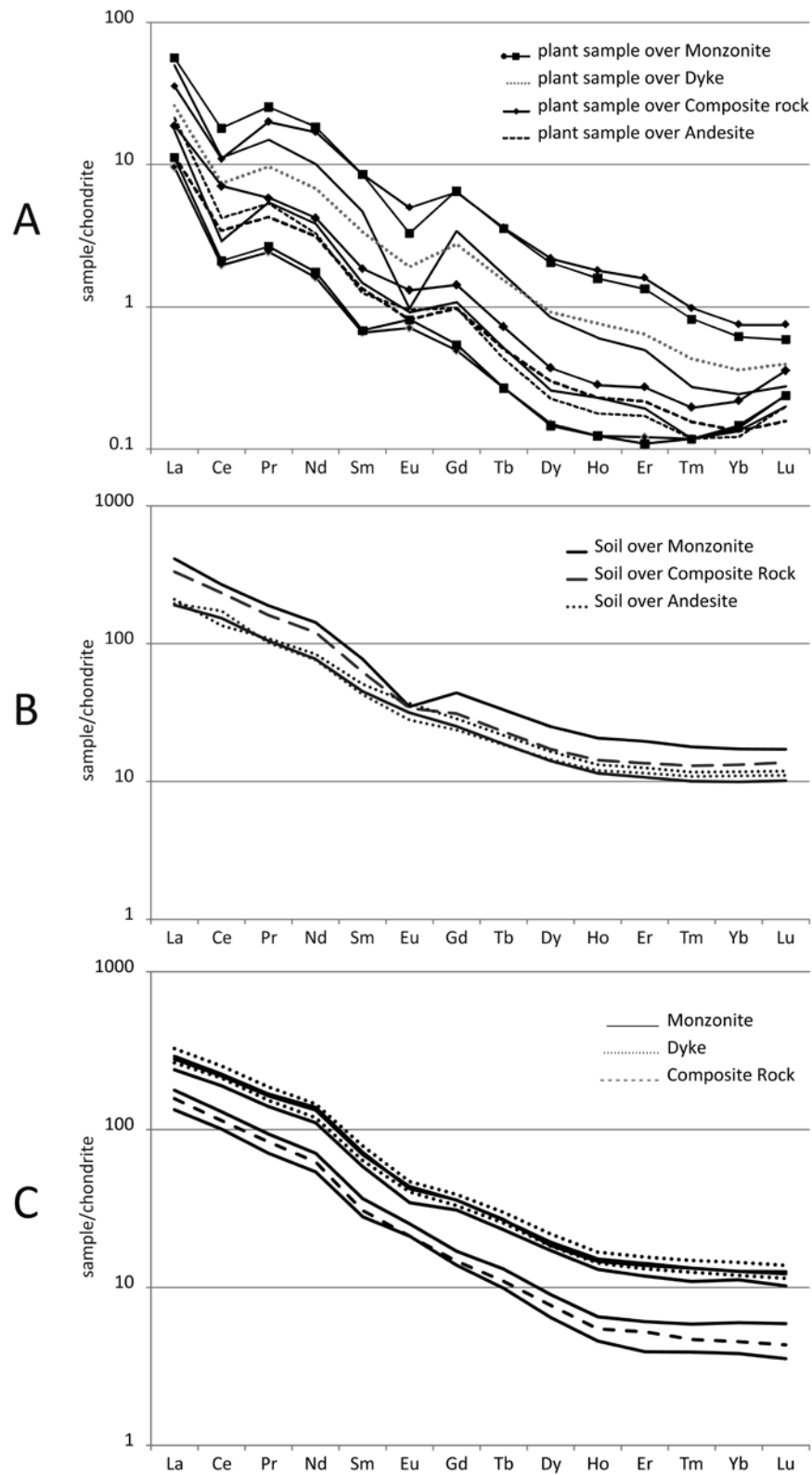


Figure 2 - Chondrite normalized REE patterns in (a) leaves of *Schinus lentiscifolius*, (b) soils, and (c) rocks from Lavras do Sul Shoshonitic Association (ASLS).

study area: they have (i) distinct Ce-negative anomalies, the (ii) HREE to LREE fractionation is higher, and (iii) plant patterns show W-type tetrad effects.

According to Evans (1990) the REE are insoluble in the form of carbonates, hydroxides, phosphates and fluorides. Shan et al. (2002) observed that the sorption of REE increase when the concentration of organic acids around the plant roots is higher. Wytttenbach et al. (1998) found Ce/Ce\* ratio (Ce\* = average of La and Pr contents) values ranging from 0.28 for ivy to 0.67 for fern, and concluded that Ce anomalies of the plant species are always lower than 1. They considered that small changes of the redox potential of the rhizosphere might have contributed to the increase of this variability. The negative anomalies probably reflect the oxidation of trivalent to tetravalent Ce, which causes the decrease of its mobility in the rhizosphere (Fu et al. 1998), and its consequent decrease of solubility in relation to other REE.

The preferential concentration of LREE by plants has been observed by several authors. Miao et al. (2007) observed that the fractionation of HREE in relation to LREE occurs during transport in the soil-plant system. According to these authors, organic acids of low-molecular weight are dominant in solubilizing LREE, so they increase their availability and consequent absorption by plants. Zhang et al.

(2002) proposed that fractionation does not occur during the absorption of REE in the rhizosphere, but during transport and deposition of REE in the vegetal tissues. Wang et al. (1997) and Ding et al. (2006) suggest that REE fractionation occurs either, in the rhizosphere or in the plant tissues, by reacting with organic ligands. A comparison of REE contents in plant and soil samples (Fig. 3) shows that LREE and MREE are more enriched than HREE in plants. Cerium is less mobilized to the plant than other LREE. Lutecium and Gd can show slight positive anomalies that can be ascribed to the tetrad effect of W-type. Europium shows a variable behavior with positive or negative anomalies that can be explained by the oxidation (Eu<sup>+++</sup> versus Eu<sup>++</sup>) in the soil/plant system.

The tetrad effect W-type observed in the plant samples reflects the higher absorption of those REE that demand more energy for forming complexes, as discussed by Sastri et al. (2003). Fu et al. (1998) proposed that the tetrad effect in plants is controlled by the form of REE ions in the absorbed solutions; therefore, it depends on the occurrence of them as organic complexes or free cations. Solutions where complexes of REE are predominant in relation to free cations will precipitate compounds with M-type patterns; when free cations are dominant, W-type patterns will be produced. Hence, according to those authors, the

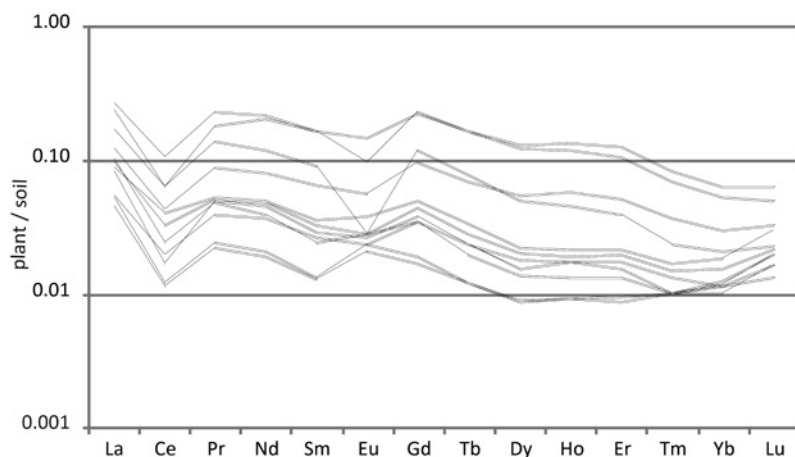


Figure 3 - REE patterns of plants normalized against the average contents in soils.

W-type patterns indicate that the REE were absorbed by the plant dominantly as free cations. As additional evidence, Fu et al. (1998) explain the negative Ce anomalies by its oxidation in the soil/plant system to tetravalent Ce, a more insoluble form that would be less absorbed by the plant.

Kovalevskii (1979) determined that the absorption of chemical elements by plants in the soil/plant system is 3,000 times higher as soluble forms than as solid phases. The W-type tetrad effect observed in the *S. lentiscifolius* in the Lavras do Sul area indicates that the soluble forms are free ions as proposed by Fu et al. (1998) for ferns.

### CONCLUSIONS

There are some general similarities in rocks, soils and plants in the Lavras do Sul area such as an approximate parallelism of chondrite-normalized REE patterns. The patterns determined in *S. lentiscifolius* samples when compared to those of soils show, however, relevant differences: LREE enrichment, negative Ce anomalies, variable behavior of Eu, and, particularly the development of W-type patterns, resulting in a tetrad effect. The W-type patterns are interpreted as indicating that REE were absorbed by *S. lentiscifolius* as simple ions rather than as complex ions or, alternatively, that the transport of REE in the plant metabolic processes was as free ions. Ce and Eu anomalies are caused by oxidation of these elements to tetra and trivalent forms, respectively, which reduces their mobility in the soil/plant system, and, consequently the Ce and Eu availability to plants. The Gd and Lu positive anomalies were observed in other plant species by other authors (Semhi et al. 2009, Lima e Cunha et al. 2009) and can be explained by the tetrad effect of W-type, as previously proposed by Fu et al. (1998, 2000) and Lima e Cunha et al. (2010). W-type patterns such as those described in this paper have been referred mainly in sea-water and minerals deposited from hydrothermal solutions. The recognition of tetrads, either, M- or W-type

patterns, is an additional tool for understanding the biogeochemistry of REE and can contribute to the study of monitoring processes of contaminated environment or to mineral prospecting.

### RESUMO

Este trabalho trata da distribuição dos ETR na rocha, solo e planta em área de ocorrência de rochas monzoníticas do extremo sul do Brasil. O padrão dos ETR em *Schinus lentiscifolius* apresenta anomalia negativa de Ce e significativo efeito tétrade, do tipo W, ausente no padrão da rocha e do solo. A configuração das curvas da rocha e do solo é similar e sem fracionamento das ETR durante a pedogênese. O padrão em W é interpretado como decorrente da absorção dos ETR pela planta na forma de íons livres e não complexados, ou, alternativamente, que o transporte das ETR nos processos metabólicos foi na forma de íons livres. O reconhecimento de tétrades, seja do tipo W ou M, é uma ferramenta adicional na compreensão da biogeoquímica dos ETR e pode contribuir para o estudo de processos de monitoramento de ambientes contaminados ou para pesquisas em prospecção mineral.

**Palavras-chave:** ETR, efeito tétrade, *Schinus lentiscifolius*, sul do Brasil.

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