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FRACTIONATION OF RARE EARTH ELEMENTS IN WEATHERING PROFILES ON PHONOLITES IN THE AREA OF LAGES, SANTA CATARINA, BRAZIL

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ABSTRACT

Niobium and rare earth elements are associated with alkaline intrusions, especially in sequences containing carbonatites.

During deep ferralitic weathering on the Lower Tertiary peneplanation plain REE are mobilized and depleted as well in the lower saprolite as in the upper ferralite, except Cerium which shows a positive anomaly.

Triangular diagrams of Ce, Nd, La represent a relative enrichment of La, whereas comparing Ce, La and Nb, the increase of Niobium is strongest with rising weathering.

After intersection of the landscape into inselbergs and lowering of the aquifers a later period of mobilization and migration of the REE together with manganese, aluminium and silica took place in descending direction. Their absolute enrichment by precipitation is concentrated in fissure fillings and porespaces in the lowermost part of the profiles. Main minerals are lithiophorite and halloysite.

RESUMO

Nióbio e elementos da família das terras raras são associados com intrusões alcalinas, especialmente em seqüências com carbonatitos.

Durante o intenso intemperismo ferralítico que afetou estas rochas, desde o Terciário inferior, os ETR foram mobilizados e lixiviados dos perfis de alteração, com exceção do cério, que apresenta uma anomalia positiva.

Diagramas triangulares Ce, Nd e La exibem um relativo enriquecimento de La, enquanto nos diagramas Ce, La e Nb, o enriquecimento de Nb é muito mais importante com a evolução do intemperismo.

Após a dissecação do relevo e o rebaixamento do aqüífero, no Quaternário, um longo período de mobilização e migração de ETR, manganês, alumínio e sílica, ocorreu para a base dos perfis. Seu enriquecimento absoluto, por precipitação, é encontrado preenchendo fissuras e espaços porais nas partes inferiores dos perfis. Os principais minerais secundários são litioforita e haloisita.

INTRODUCTION

The phonolite complex of Lages, SC, Brazil (Fig. 1) is dated with 65 to 75 Ma (Amaral *et al.*, 1967; Scheibe *et al.*, 1985). The magmatic sequence penetrated Paleo-Mesozoic clastic sediments and the Lower Cretaceous complex of the Paraná basalt. The magmatism is related to lineament structures, which opened during the time of sea floor spreading of the Atlantic ocean.

FRESH ALKALINE ROCKS

The petrography of the fresh rocks is described by Lindstaed (1972), Szubert & Vegara (1975) and Scheibe *et al.* (1984).

The agpaitic alkaline rocks are differenciated into analcime trachytes, phonolites, porphyritic nepheline syenites in the SE part and porphyritic phonolites in the NW part of the district. Olivine melilitite and olivine nephelinite are ultrabasic alkaline rocks. The phonolites are fine-grained to porphyritic in texture. Scorza (1965) also describes a small outcrop of ultrabasic alkaline rocks (olivine melilitite) east of Cerro Alto. Ankerite carbonatites are present in Fazenda Varela (Scheibe, 1976, 1979).

The fine-grained phonolites are characterized by submillimetric alkali feldspars, nepheline and aegirine-augite crystals, sodalite, albite and some rare accessory sodium minerals containing Ti and Zr, including:

Eudialyte (Ca, Na, *Ce*)$_5$ (Zr, Fe)$_2$ Si$_6$ (O, OH, Cl)$_{20}$
Lavenite (Na, Ca, Mn, Fe)$_3$ (Zr, *Nb*, Ti) (Si$_2$O$_7$) (OH, F)
Murmanite Na$_2$MnTi$_3$ (O/Si$_2$O$_7$)$_2$ ± 8H$_2$O
Astrophyllite (K$_2$, Na$_2$, Ca) (Fe, Mn)$_4$ (Ti, Zr) (OH/Si$_2$O$_7$) and
Neptunite Na$_2$FeTi (Si$_4$O$_{12}$) (Scheibe *et al.*, 1984)

The porphyritic phonolites are characterized by prismatic alkali feldspar, idiomorphic nepheline, aegirine and sodalite. They are situated in the Farinha Seca section and in local smaller outcrops.

SUPERGENE ALTERATION

The supergene alteration is polyphasic and polygenetic. The initial ferralitic weathering was related to the topographically low lying Sulamericano plain which is presumed to be Lower Tertiary in age. Due to tectonic uplift during Upper Tertiary and Quaternary time the rolling landsurface is actually situated at an altitude between 850 and 920 m including the Morro do Tributo (1167 m). Due to tectonic and climatic change the Lower Tertiary weathering profiles are superimposed by younger alteration processes (Valeton *et al.*, 1988).

Bauxite deposits, as a product of the ferralitic weathering, are located in the northern part of the area on phonolites and also on diabase in Agua Branca and Farinha Seca. Only on hilltops between 850 to 920 m they are preserved.

The terrain is incised by younger valleys, which are totally free of *in-situ* bauxite and the recent morphology cuts the bauxites. In the profiles all gradations from kaolin to bauxite ("aluminous kaolin", "kaoliniferous bauxite", classification after Aleva, 1984) are presented in lenticular layers (Fig. 2). The distribution pattern of the various bauxite grades seems to follow a fossil drainage system.

Oliveira (1985) describes the initial alteration of aegirine into goethite. The transformation of the feldspar into gibbsite started along the cleavages pattern. Nepheline altered into well crystallized gibbsite.

The high porosity of the bauxite (up to 60%) is caused by a variation of pores and elongated holes, forming a skeletal network (spongy, cellular), which provokes extremely good drainage conditions. The major part of the clay fraction is kaolinite. Small quantities of boehmite may occur. Accessory minerals are zircon and anatase.

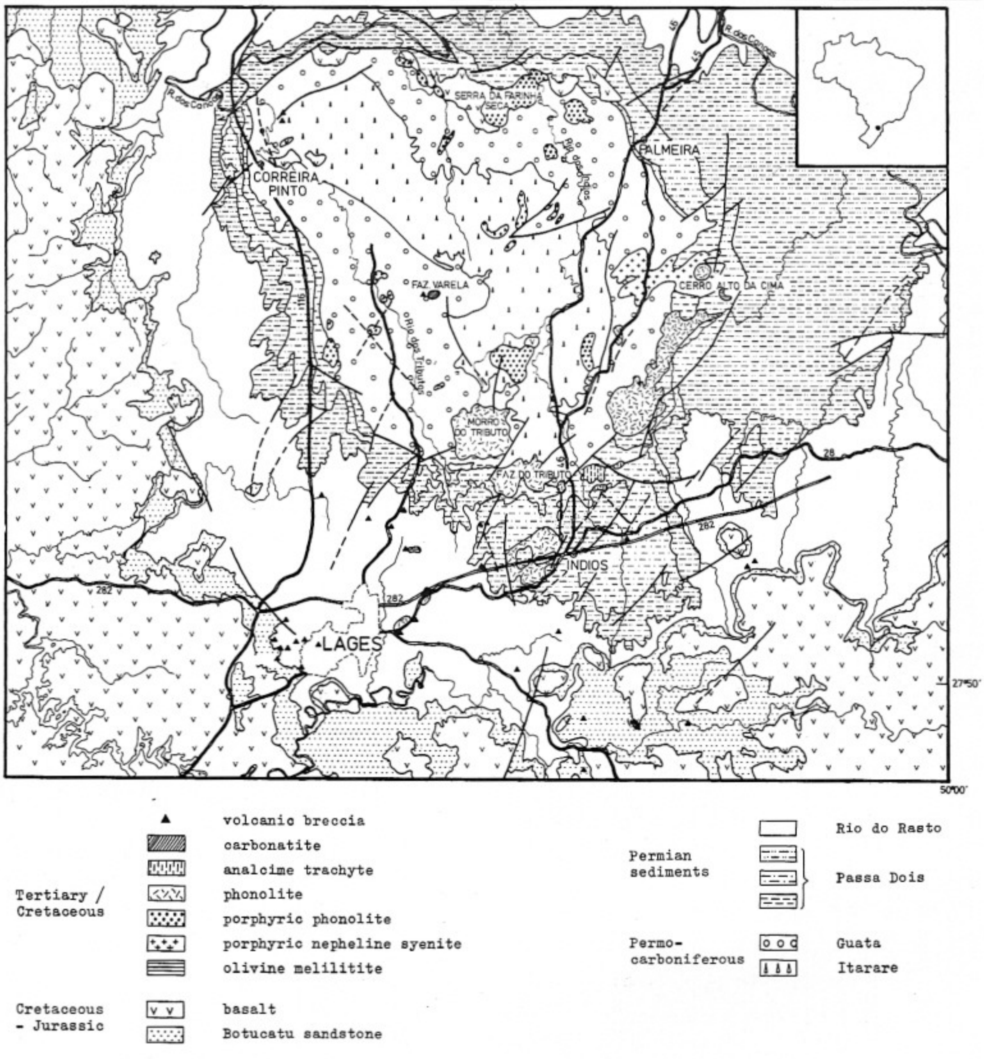


Figure 1 — Geological map of the Lages area (after Scheibe *et al.*, 1984).

Polygenetic alteration led either to erosion and truncation of exposed profiles or to a cover by irregular dusky dark red and soft laterites, which have to be dated as younger than the bauxite but older than the superimposed acidic podsolic soil of the Quaternary (Fig. 3). An active degradation of the topmost part of the bauxite is realized by its solution and breakdown to a residual breccia. The downward mobilization led to a precipitation of poorly crystallized kaolinite, several generations of halloysite, silica and black material rich in lithiophorite and in REE. Detailed mineralogical and chemical data are given in Valeton *et al.* (1988).

FRACTIONATION OF REE IN THE WEATHERING PROFILES

The determination of the REE was partly done by the GEOSOL Laboratory, Belo Horizonte (31 samples) and by the Hahn-Meitner-Institut, Berlin (26 samples) by ICP.

Schroll (1979) subdivided two categories of elements in bauxites:

1. bauxitophilic elements:
   Al, Ga, Ti, Zr, V, Nb, Cr,
   Mo (W)
2. other elements:
   Si
   Fe, Mn, Ni, Co
   Li, Be, B, Sn
   Ca, Cr, Ba, Sc, Y, La, Th, U
   Cu, Pb, Zn

The REE display very similar behavior in all geochemical processes because of their similar chemical properties. The behavior of REE in chemical weathering processes is not yet well documented.

Nesbitt (1979) published a paper on the distribution and fractionation of REE in a weathering profile on granodiorite. He assumed TiO_2 was immobile during alteration and analysed an enrichment of the HREE (to + 300%) in contrast to the LREE (+ 100 to + 200%). He concluded that the REE have been transported into the system along the fractures. The weathering scheme (solution-transport-precipitation) is controlled by the pH and Eh.

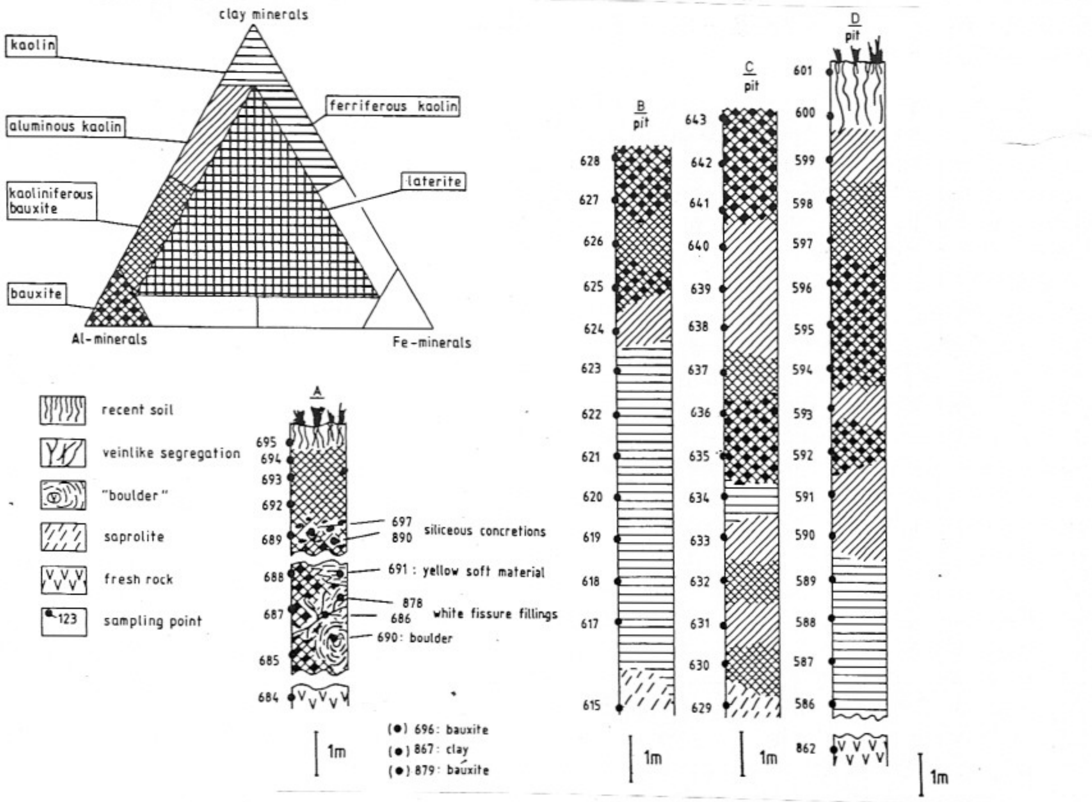


Figure 2 — Schematic description of the weathering profiles on phonolite, classified after Aleva (1984). A, loc. 11, Farinha Seca, quarry; B, loc. 5, Farinha Seca, pit 42; C, loc. 6, Farinha Seca, pit 20; D, loc. 3, Barreiros.

First detailed examinations of REE in European karst bauxites originated from Bardossy *et al.* (1976), Vukotic *et al.* (1981, 1983), Maksimovic *et al.* (1976, 1983) and Dragovic *et al.* (1985). Several phases of reworking, transportation and sedimentation in environments with changing pH and Eh conditions let to deposition of either red bauxites or mottled bauxites with preserved red parts under hydromorphic conditions to white bauxite (Vukotic *et al.,* 1983). Red bauxite of Montenegro possesses higher contents of Σ REE and Σ LREE and often a marked positive Cerium-anomaly whereas white bauxites tend to show a stronger negative Europium-anomaly. The higher solubility and mobility of the HREE in alkaline solutions leds to their relative enrichment in white bauxites (Dragovic *et al.*, 1985) (Table 1, Fig. 4). Authigenic

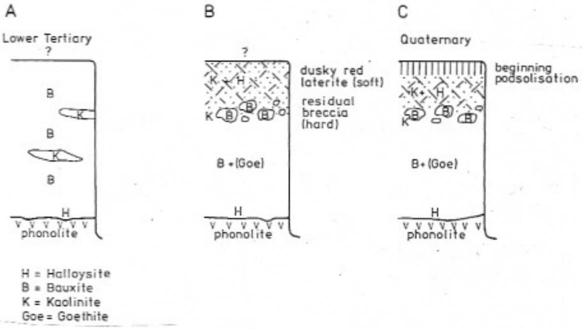


Figure 3 — Stepwise supergene alteration since the: A, initial ferralitisation during Lower Tertiary time; B, subsequent formation of a residual breccia on top of the bauxite, overlayn by a dusky red latosol; C, Quaternary beginning podsolisation.

minerals of REE of the bastnaesite group with the idealized formula: $(Ce, La, Nd...)(CO_3)F$ like synchysite - (Nd), batnaesite - (La), bastnaesite - (Ce) and bastnaesite - (Nd) were described in bauxites from Hungaria, Montenegro and Yugoslawia. Phosphates of the monazite - group with the empirical formula $(P_{3.64}S_{0.17})_{3.81}(Nd, La, Ce...)_{4.04}Ca_{0.29}$ and Nd - goyazite with the empirical formula $Ca_{0.26}Sr_{0.45}REE_{0.33}Al_{3.01}(PO_4)_{1.85}(SO_4)_{0.14}(OH)_{6.35}$ were detected in mediterranian bauxites by Maksimovic *et al.* (1983).

REE IN THE FERRALITIC WEATHERING PRODUCTS OF ALKALINE ROCKS OF THE LAGES AREA

Using the concentration ratios $C_{laterite}/C_{phonolite}$ (after Mackenzie & Murata, 1952) the relative gains and losses of the major and minor elements as well as of the REE can be determined relative to the parent rock (Tables 2-4). The elements Al, Ti, Ga, Ni, Pb, Th, V and Ce have been enriched in the bauxite and the yellow soft material. Iron, as well as Y and Yb, have only been enriched in the bauxite and in the yellow material (sample 691). Manganese is exclusively enriched with the halloysite in the white fissure filling which is often combined with the manganese phases (sample 686). Yb and Lu increase in the yellow soft material, and they are only slightly leached in the bauxite (concentration ratios Yb, 0.99; Lu, 0.94; sample 692). All REE were leached with exception of Ce. The study of the chondrite normalized graphics (Figs. 5a-d) show a higher content of the LREE in regard to the HREE which is also apparent in the fresh rock. In all profiles the REE behave differently in the bauxite than in the rest of the profile. The bauxite possesses lower values of REE. In contrast to the bauxite, the REE increase in the deeper parts of the profiles. In the saprolites (Figs. 5b, c) at the base of the profiles the REE are strongly enriched.

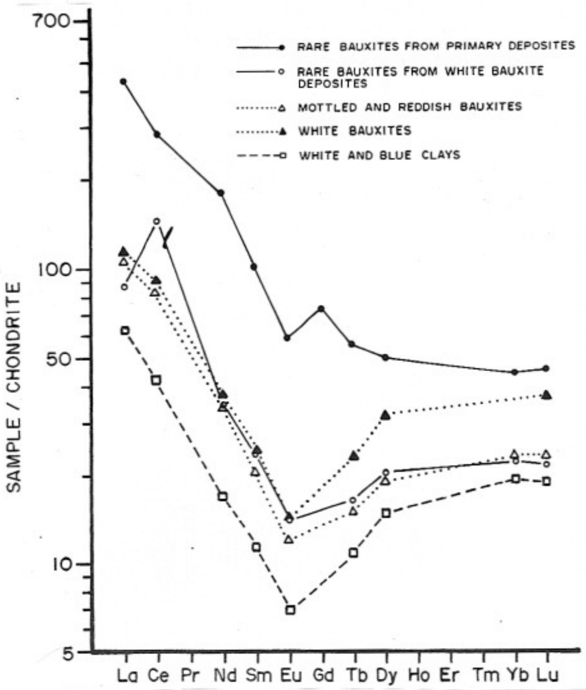


Figure 4 — Chondrite normalized REE - distribution patterns in Karst - bauxites of Montenegro (Dragovic *et al.*, 1985).

A strong positive Ce-anomaly is very obvious in all chondrite normalized graphs. This anomaly can partly be explained by the high content of Ce in the fresh phonolite. This Ce-content is enriched during alteration. This may be explained by the oxidation state of Ce (IV) in contrast to the ideas of Bonnot-Courtois (1981).

The behavior of the REE in location 11, Farinha Seca (Fig. 5a), is interesting because the fresh phonolite shows no Ce-anomaly but a

Table 1 — Characteristics of rare earth elements distribution patterns in Karst-bauxites of Montenegro (Dragovic *et al.*, 1985).

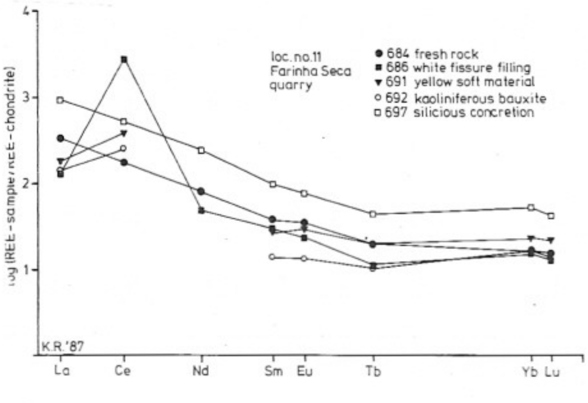
Lithological type	(ΣREE) (ppm)	(ΣLREE)* (ppm)	(HREE)** (ppm)	$\left(\frac{\Sigma LREE}{\Sigma HREE}\right)$	$\left(\frac{La}{Sm}\right)$	$\left(\frac{Yb}{Tb}\right)$	$\left(\frac{Eu}{Sm}\right)$	Eu/Sm range
Red bauxites from primary deposits*** (4 samples)	594.2	530.1	64.1	8.5	6.9	3.6	0.21	0.21 ÷ 0.22
Red bauxites from white bauxite deposits (6 samples)	171.7	147.2	24.5	6.5	6.1	5.9	0.22	0.21 ÷ 0.24
Mottled and pink (5 samples)	158.8	134.8	24.0	5.6	9.0	7.1	0.22	0.20 ÷ 0.24
White bauxites (8 samples)	183.5	146.0	37.5	3.8	7.6	7.1	0.23	0.20 ÷ 0.25
White and blue clays (6 samples)	89.3	71.0	18.3	4.0	9.1	7.7	0.23	0.21 ÷ 0.27

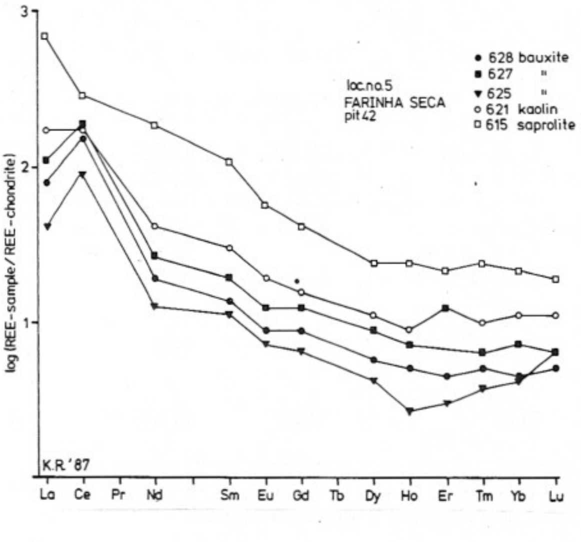
* Light rare earth elements $\Sigma LREE = La+Ce+Pr+Nd+Sm+Eu$
** Heavy rare earth elements $\Sigma HREE = Gd+Tb+Dy+Ho+Er+Tm+Yb+Lu$
*** White bauxite source material

Table 2 — Determination of the REE in the weathering products on phonolites (ppm).

	Sample	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Loc. 3	586	66.4	465.4	27.1	7.0	1.8	7.1	n.d.	5.7	1.1	3.3	0.71	3.7	0.57
	590	66.6	162.0	15.0	4.22	1.65	n.d.	0.81	n.d.	n.d.	n.d.	n.d.	5.2	0.544
	594	68.5	148.6	21.4	4.0	0.85	2.6	n.d.	2.1	0.41	0.83	0.21	0.99	0.15
	597	87.2	150.6	24.8	7.8	2.3	6.5	n.d.	7.5	1.4	4.4	0.80	5.0	0.70
	598	65.2	194.2	22.2	6.2	1.6	5.5	n.d.	5.6	1.1	3.5	0.66	4.0	0.58
	601	69.8	269.7	19.8	5.3	1.5	5.0	n.d.	4.8	0.98	3.1	0.59	3.4	0.47
Loc. 4	603	28.1	140.0	28.0	6.16	2.26	n.d.	1.01	n.d.	n.d.	n.d.	n.d.	3.06	0.421
	605	56.9	502.0	41.0	8.4	3.06	n.d.	1.76	n.d.	n.d.	n.d.	n.d.	6.84	0.94
	609	34.0	1680.0	n.d.	6.18	2.5	n.d.	1.3	n.d.	n.d.	n.d.	n.d.	6.2	0.835
	612	55.6	181.0	n.d.	6.29	2.2	n.d.	1.19	n.d.	n.d.	n.d.	n.d.	6.04	0.787
Loc. 5	615	186.1	210.4	98.8	17.9	3.5	9.2	n.d.	6.6	1.4	3.8	0.62	3.6	0.52
	621	43.0	121.4	20.2	5.1	1.2	3.3	n.d.	3.1	0.54	2.2	0.28	2.0	0.29
	623	30.3	475.0	13.0	2.9	1.04	n.d.	0.52	n.d.	n.d.	n.d.	n.d.	2.23	0.304
	625	10.9	62.9	6.4	1.7	0.44	1.4	n.d.	1.1	0.16	0.54	0.10	0.71	0.18
	627	28.3	136.8	13.0	3.2	0.79	2.6	n.d.	2.3	0.43	2.2	0.17	1.2	0.18
	628	21.9	100.5	9.2	2.3	0.53	1.9	n.d.	1.6	0.32	0.81	0.13	0.84	0.15
Loc. 6	629	65.2	347.5	25.8	6.4	1.5	5.2	n.d.	4.4	0.81	3.0	0.54	3.3	0.51
	630	43.9	140.0	20.0	4.83	2.16	n.d.	1.18	n.d.	n.d.	n.d.	n.d.	4.92	0.657
	631	33.5	258.3	16.0	5.2	1.4	4.8	n.d.	4.6	0.92	3.4	0.50	3.0	0.42
	636	12.6	62.3	5.6	1.6	0.44	1.5	n.d.	1.2	0.22	0.65	0.09	0.58	0.18
	640	106.0	659.0	n.d.	6.91	2.6	n.d.	1.23	n.d.	n.d.	n.d.	n.d.	7.81	1.16
	641	13.9	91.0	9.5	3.1	0.90	3.0	n.d.	3.2	0.62	2.5	0.49	3.2	0.59
	643	58.4	270.2	18.4	5.6	1.6	5.3	n.d.	5.3	1.2	3.9	0.63	3.9	0.55
Loc. 7	645	78.1	258.0	22.0	3.82	1.38	n.d.	0.78	n.d.	n.d.	n.d.	n.d.	3.78	0.475
	650	46.2	177.0	21.0	5.37	2.03	n.d.	1.16	n.d.	n.d.	n.d.	n.d.	4.56	0.689
	651	37.8	161.0	28.0	5.68	2.3	n.d.	1.21	n.d.	n.d.	n.d.	n.d.	5.4	0.774
Loc. 9	662	120.0	280.0	73.0	12.5	4.1	n.d.	1.68	n.d.	n.d.	n.d.	n.d.	6.13	0.872
	665	69.3	241.0	45.0	8.6	2.75	n.d.	1.3	n.d.	n.d.	n.d.	n.d.	5.73	0.844
	668	177.0	331.0	73.0	9.82	2.86	n.d.	1.19	n.d.	n.d.	n.d.	n.d.	5.4	0.832
	673	143.0	280.0	34.0	7.37	2.67	n.d.	1.6	n.d.	n.d.	n.d.	n.d.	6.63	0.99
	675	118.0	285.0	26.0	6.03	2.38	n.d.	1.1	n.d.	n.d.	n.d.	n.d.	5.96	0.805
	865	85.0	313.0	40.0	8.8	2.57	n.d.	1.13	n.d.	n.d.	n.d.	n.d.	3.52	0.46
Loc. 11	684	108.0	166.0	49.0	7.61	2.57	n.d.	0.99	n.d.	n.d.	n.d.	n.d.	3.2	0.485
	686	42.3	2620.0	30.0	6.02	1.72	n.d.	0.58	n.d.	n.d.	n.d.	n.d.	2.95	0.403
	691	57.7	364.0	n.d.	5.44	2.14	nd.	0.98	n.d.	n.d.	n.d.	n.d.	4.3	0.658
	692	45.2	237.0	n.d.	2.75	0.984	n.d.	0.52	n.d.	n.d.	n.d.	n.d.	3.19	0.457
	697	296.0	491.0	146.0	19.8	5.69	n.d.	2.23	n.d.	n.d.	n.d.	n.d.	10.1	1.32

smooth positive Eu-anomaly. The same distribution is represented in the siliceous concentration (sample 697) only with a higher content. In the bauxite there is a positive Ce-anomaly similar to that in the yellow soft material. But in the halloysite fissures there is a very strong positive Ce-anomaly. In regard to the fresh rock all REE-contents are depleted in the bauxite whereas in the soft yellow material (sample 691) there is an increasing content of REE. The soft material is characterized by a high content of SiO_2 as well as of Nb. To indicate the similarities in behavior during alteration, cluster analyses were computed separately for the bauxites and the kaolinites (see Figs. 6a, b). In the cluster analyses of the kaolinites (Fig. 6a) three main





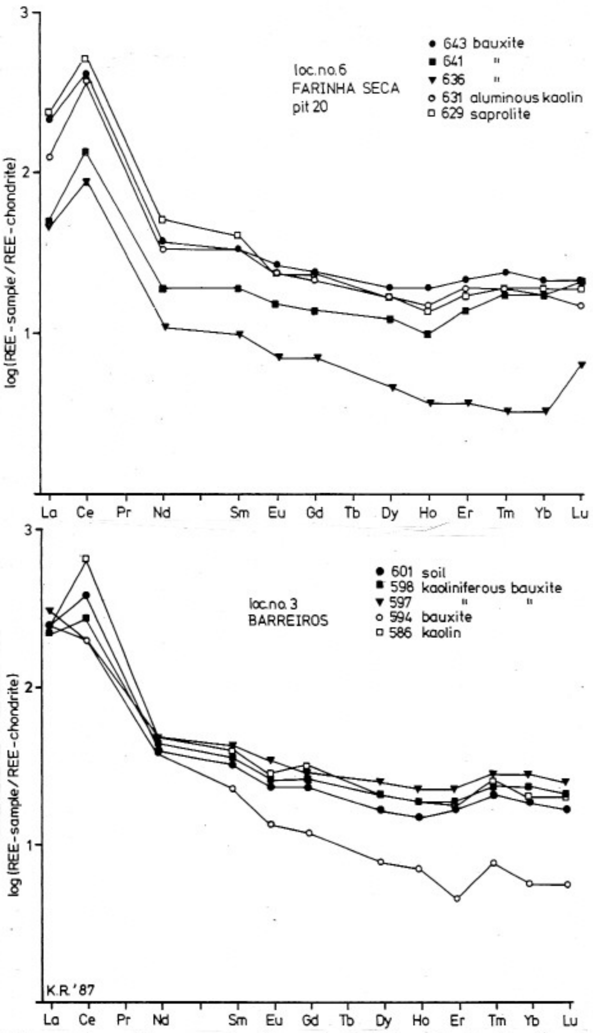


Figure 5 — Rare earth element distribution in the fresh rocks, saprolite, kaolin, bauxite and fissure filling of the Lages area. A) loc. 11, Farinha Seca; B) loc. 5, Farinha Seca; C) loc. 6, Farinha Seca; D) loc. 3, Barreiros (data after Retzmann).

Table 3 — Enrichment factors relative to the fresh phonolite (*Claterite/Cphonolite;* data after Retzmann).

	Halloysite	Yellow soft material	Bauxite	Siliceous concretion
Si	0.67	0.27	0.42	1.34
Al	1.89	2.35	2.05	0.52
Fe	0.92	1.86	2.62	0.59
Mn	1.65	0.5	0.4	0.5
K	0.01	0.01	0.03	1.61
Ti	1.19	2.45	4.19	1.52
P_2O_5	1.33	3.0	3.66	19.6
Ba	0.55	0.15	0.18	9.06
Ga	1.65	2.69	2.13	
Ni	2.36	1.14	1.71	1.57
Pb	8.09	2.0	2.13	0.65
Sr	0.004	0.04	0.05	4.22
Th	1.72	3.08	1.82	
V	1.18	2.24	4.79	2.18
Y	0.5	1.25	1.0	2.97
Zn	0.64	0.56	0.59	0.29
Zr	0.88	1.49	1.26	1.82
La	0.55	0.55	0.56	2.11
Ce	15.15	2.05	1.62	2.41
Nd	0.5	0.49		2.63
Sm	0.79	0.71	0.36	2.60
Eu	0.66	0.83	0.38	2.21
Tb	0.58	0.99	0.52	2.25
Yb	0.92	1.34	0.99	3.16
Lu	0.83	1.36	0.94	2.72

groups are expressed. The first group comprises the HREE represented by Gd, Tm, Dy, Ho, Er. This special group shows a very close interrelationship, but not with other elements. The second group is a very large one which includes Fe_2O_3, TiO_2, Nb, Zr, V, P_2O_5 and the REE-pairs Yb, Lu and Sm, Eu as well as Tb. The combination of the REE with the iron may be deduced from the iron rich primary minerals, for example, aegirine and eudialyte which contain REE in their structure. The last group contains Al_2O_3, Ce, Mn. These elements may express the association of cerium with manganese minerals. Cerium and manganese show a relative strong correlation (Table 5). In the cluster analyses of the bauxites (Fig. 6b) there are five main subdivided groups. The first group is identical with the first group of the kaolinite cluster: the intermediate REE which seem to be independent in their behavior from the other elements. The second group are the bauxitophile elements Al, Ga, Th, Nb, Zr which become enriched during alteration. Lanthanum in the third small group is correlated with P_2O_5 as explained by Rosenberg (in Valeton, 1988). The REE-pairs Yb, Lu and

Table 4 — Characteristics of rare earth element patterns.

Lithological type	ΣREE (ppm)	ΣLREE* (ppm)	ΣHREE** (ppm)	$\left(\frac{\Sigma LREE}{\Sigma HREE}\right)$	$\left(\frac{La}{Sm}\right)$	$\left(\frac{Yb}{Tb}\right)$	$\left(\frac{Eu}{Sm}\right)$	Eu/Sm range
Kaolin (2 samples)	396.2	379.3	16.9	20.9	8.9	n.d.	0.24	0.23–0.26
Aluminous kaolin (7 samples)	672.1	664.1	n.d.	n.d.	13.3	5.0	0.37	0.33–0.40
Kaoliniferous bauxite (7 samples)	297.0	290.2	n.d.	n.d.	10.7	4.4	0.37	0.32–0.45
Bauxite (7 samples)	180.3	171.0	9.3	17.7	9.2	n.d.	0.25	0.21–0.29

* LREE, La+Ce+Nd+Sm+Eu; ** HREE, Gd+Dy+Ho+Er+Tm+Yb+Lu
n.d., not all HREE are determined

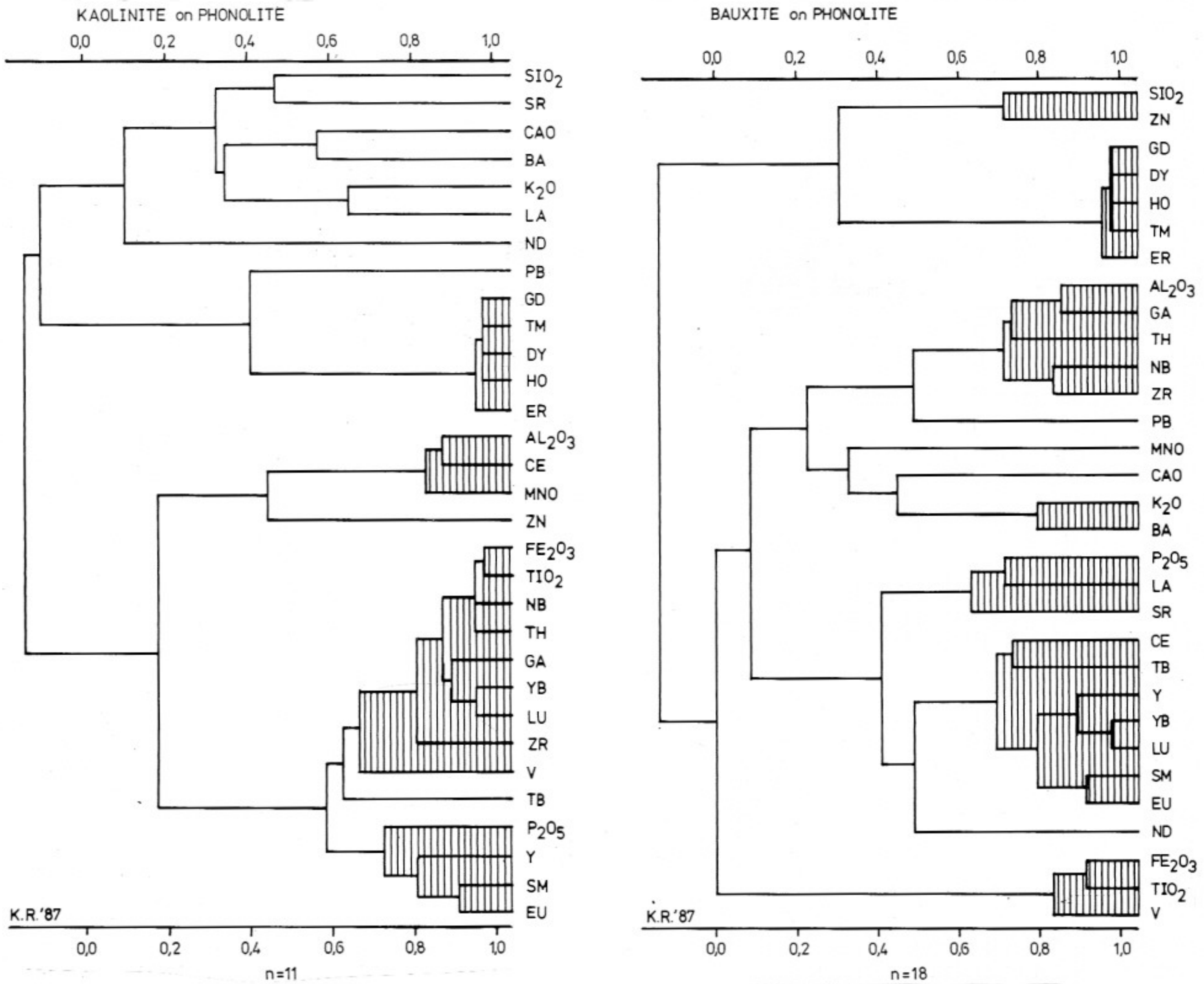


Figure 6 — Cluster analyses: A) kaolinite on phonolite; B) bauxite on phonolite (data after Retzmann).

Sm, Eu are combined with Y, Tb and Ce. They show no strong correlation with other elements. The last group is represented by Fe_2O_3, TiO_2 and V which replace each other isomorphously.

To show the relationships among Ce, La, Nb and Nd, distribution diagrams have been established. In the triangular diagram Ce-La-Nb (Fig. 7a) there is an increasing concentration of Nb during weathering in bauxites. In the system Ce-La-Nd (Fig. 7b), La possesses a rising trend. Kaolinitic rocks (rich in SiO_2) show the same trend in the system Ce-La-Nd (Fig. 7d) and in the system Ce-La-Nb (Fig. 7c) for La and Nb. Both groups, the bauxites and the kaolinites, are characterized by the same trends in the systems Ce-La-Nd-Nb during alteration but for the kaolinitic samples the fields are more widespread and the trends are not so clearly developed.

Table 5 — Correlation diagram of elements in bauxites, Lages area (after Rosenberg, 1986).

	Al	Fe	Mn	Ca	K	Ti	P	L.I.	Ba	Ce	Ga	La	Nb	Nd	Pb	Sr	Th	V	Y	Zn	Zr
Si	−0.98	−0.79	+0.25	+0.31	+0.60	−0.78	+0.12	−0.99	+0.57	+0.18	−0.87	+0.31	−0.70	+0.34	+0.06	+0.33	−0.76	−0.62	+0.33	+0.67	−0.61
Al		+0.73	−0.30	−0.42	−0.60	+0.70	+0.24	+0.97	−0.60	−0.16	+0.83	−0.31	+0.63	−0.36	−0.03	−0.40	+0.73	+0.53	−0.32	−0.63	+0 52
Fe			−0.25	−0.25	−0.40	+0.93	+0.34	+0.77	−0.49	−0.16	+0.88	−0.29	+0.86	−0.33	−0.08	−0.29	+0.79	+0.72	−0.20	−0.50	+0.72
Mn					+0.07	−0.21	−0.13	−0.26	+0.17	+0.47	−0.13	+0.21	−0.12	+0.41	+0.08	−0.01	−0.15	−0.19	+0.35	+0.47	−0.20
Ca					+0.83	−0.11	+0.48	−0.31	+0.66	+0.22	−0.31	+0.31	−0.09	+0.44	−0.13	+0.87	−0.31	+0 09	+0.22	−0.10	+0.19
K						−0.27	+0.21	−0 53	+0.58	−0.02	−0.42	+0.30	−0.21	+0.45	−0.18	+0.66	−0.47	−0.08	+0.16	+0.16	+0.07
Ti							+0.41	+0.76	−0.39	−0.15	+0.89	−0.21	+0.92	−0.24	−0.09	−0.15	+0.76	+0.74	−0.17	−0.55	+0.82
P								+0.32	+0.30	−0 04	+0.23	+0.42	+0.35	+0.36	−0.15	+0.59	+0.28	+0.39	+0.23	−0.41	+0.44
L.I.									−0.55	−0.16	+0.84	−0.31	+0.66	−0.34	−0.06	−0.31	+0.74	+0.62	−0.32	−0.66	+0.57
Ba										+0.48	−0.58	+0.38	−0.35	+0.51	−0.12	+0.80	−0.59	−0.14	+0.35	+0.42	−0.26
Ce											−0.14	+0.12	−0.16	+0.10	+0.21	+0.04	−0.09	−0.02	+0.16	+0.22	−0.19
Ga												−0.33	+0.84	−0.34	−0.04	−0.38	+0.76	+0.66	−0.27	−0.56	+0.70
La													−0.20	+0.80	−0.08	+0.44	−0.18	−0.19	+0.45	+0 09	−0.08
Nb														−0.18	−0.07	−0.16	+0.74	+0.63	−0.09	−0.43	+0.82
Nd															−0.08	+0.51	−0.24	−0.18	+0.53	+0.21	−0.05
Pb																−0.11	+0.07	−0.19	+0.45	−0.02	−0.12
Sr																	−0.36	+0.08	+0.35	−0.02	+0 02
Th																		+0.43	−0.08	−0.53	+0.61
V																			−0.21	−0.45	+0.58
Y																				+0.26	−0 05
Zn																					−0.57

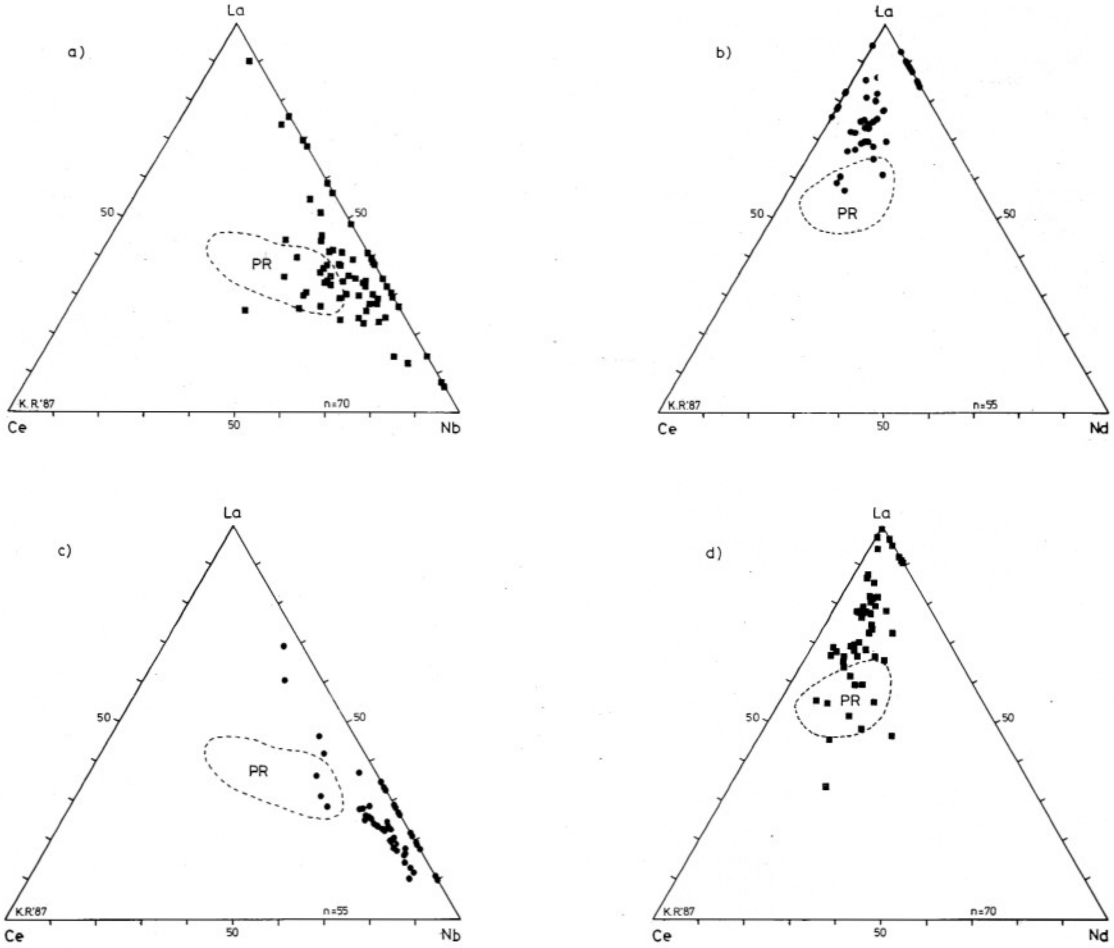


Figure 7 — Triangular diagrams: A) La, Ce, Nb in bauxite; B) La, Ce, Nd in bauxite; C) La, Ce, Nb in kaolinite; D) La, Ce, Nd in kaolinite (date after Retzmann).

CONCLUSIONS

The REE are mobilized first during the initial Lower Tertiary weathering process and second during a younger reactivation in Quaternary time.

1. In the fresh rock (phonolite) LREE were enriched opposite to HREE. During supergene alteration a mobilization and fractionation of rare earth elements took place.
2. In the alteration profiles of phonolites a very strong enrichment of Ce happened during initial weathering.
3. The bauxites are strongly depleted in REE in regard to the saprolites.
4. The REE: Gd, Dy, Ho, Er and Tb are highly positively correlated to each other and seem to be an independent group.
5. In the systems Ce-La-Nd respectively Ce-La-Nb the bauxites and the "kaolinites" show similar trends of either relative enrichment of niobium or lanthanum. But for the bauxites the variation of the data range over a more narrow field.
6. During late weathering REE are mainly concentrated in the fissures associated almost entirely with lithiophorite.
7. The REE show a behavior similar to P_2O_5, Mn and some other elements which are mobilized in late stages.

This contribution provides a brief overview of the distribution and fractionation of the REE and Nb in bauxites and SiO_2 rich weathering products on phonolites in the area of Lages, Santa Catarina, Brazil, represents the general behavior of these elements during ferralitic weathering.

More detailed mineralogical and geochemical data are needed to find out the significant primary and secondary minerals and the location of Nb and REE in their structure and the chemical processes and mechanisms which produce solution-transport-precipitation and neoformation of minerals of the REE.

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