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FERRUGINOUS BAUXITE FROM NAZARÉ PAULISTA (SÃO PAULO, BRAZIL): GEOCHEMICAL EVOLUTION

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The bauxite deposits of Nazaré Paulista are the lateritization result of meta-basic (amphibolitic) rocks. In this paper the alterations of major, trace, and rare earth elements during that process were traced up. It was found that the weathering led to the formation of an alteration blanket on the mountainous slopes of the region, with iron rich bauxites on tops and upper slopes, and clay at the lower levels. The distribution of the various elements was investigated, and is presented by tables and figures.

* * *

ŽELJEZOVITI BOKSITI PODRUČJA NAZARÉ PAULISTA — GEOKEMIJSKA EVOLUCIJA

Boksitna nalazišta područja Nararé Paulista rezultat su lateritizacije meta-bazičnih (amfibolitskih) stijena. U ovom su radu proučavane promjene kojima su za vrijeme tog procesa bili podvrgnuti vodeći elementi, elementi u tragovima te elementi rijetkih zemalja. Nadeno je da je proces raspadanja prouzrokovao tvorbu promjenljivog pokrova na brdovitim padinama područja, sa željezovi-tim boksitima po vrhovima i gornjim padinama i glinom na donjim nivoima. Raspodjela različitih elemenata ispitana je i prikazana tabelama i slikama.

(R. M.)

INTRODUCTION

The Nazaré Paulista bauxite deposit is located in south eastern Brazil, State of São Paulo, 45 km northeast of the city of São Paulo (Fig. 1).

The morphology of the region consists of ridges up to 130 m above sea level, dissecated by a high density drainage network. The climate is tropical, with no dry season. Mean annual temperature is about 20 °C and annual rainfall oscillates between 1400 and 1500 mm.

At Itaberaba Ridge, where the deposit is situated, the Itaberaba Group outcrops. It is a Proterozoic volcano-sedimentary sequence comprised of metabasic rocks (metaigneous and metatuffaceous rocks of basic to intermediate composition), calc-silicate rocks (metamarls and metadolomites) and metapelitic rocks (sericite schists). A granitic intrusion cutting the sequence transformed the nearby lithologies into hornfels [2, 3, 4].
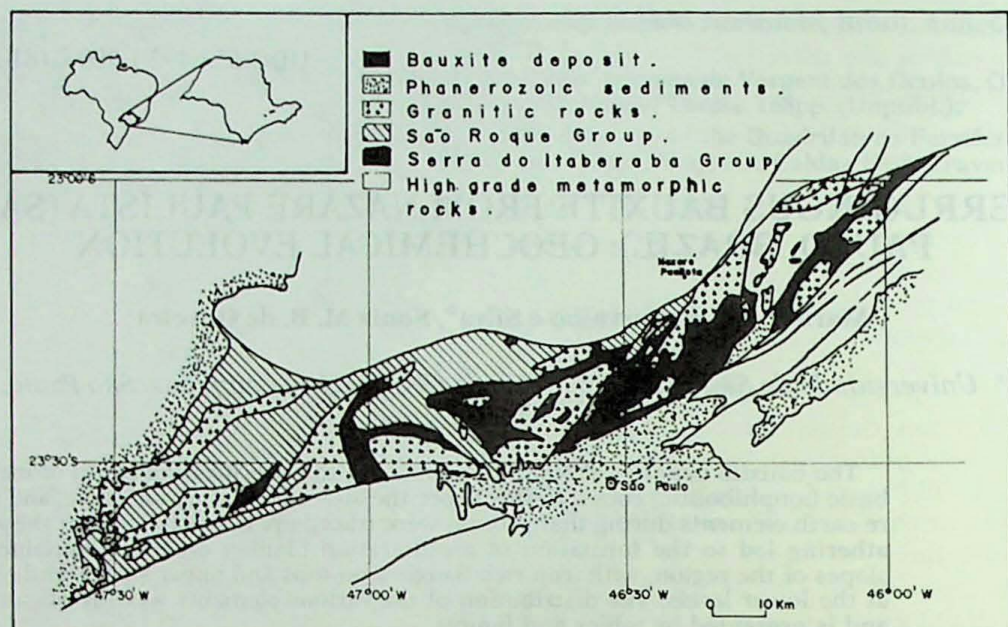
Fig. 1. Geologic map of Nazaré Paulista region. After **JULIANI** et al. [4]

The bauxite deposit was formed by the lateritization of the metabasic rocks (amphibolites) in top and slope topographic positions. First prospection work of the ore deposit was carried out by the Institute of Technological Research of São Paulo (IPT). Detailed information about the main features of the deposit was given by **Beljavskis** et al [1]. Estimated reserves amont 5.6 10^6 tons distributed in several ore bodies, with mean contents of 34,8 % of Al_2O_3, 28,8 % of Fe_2O_3 and 7,7 % of reactive SiO_2. The mean thickness of the bauxite layer is 2.6 m.

This paper is concerned with the behavior of major, trace and rare earth elements during the amphibolite bauxitization.

MATERIALS AND METHODS

Forty four samples of bauxite and related products (clay) were taken from five pits dug in the ore body. Table 1 shows the depth, topographic position and number of samples for each pit. The alteration profile in top and upper slope positions consists essentially of bauxite (pits A and B). Towards lower slope positions (pits C, D and E) clay predominates over bauxite. Three samples of bauxite were taken from outcrops near pits B and C. The mineral phases, gibbsite, goethite and kaolinite and minor amounts of quartz, litiophorite, anatase and hematite, present in 47 samples, were ascertained by X-ray diffraction.

The fresh rock was sampled in three outcrops. Microscopical examination reveals hornblende and plagioclase as main constituents, and quartz, chlorite and titanite as accessory minerals.

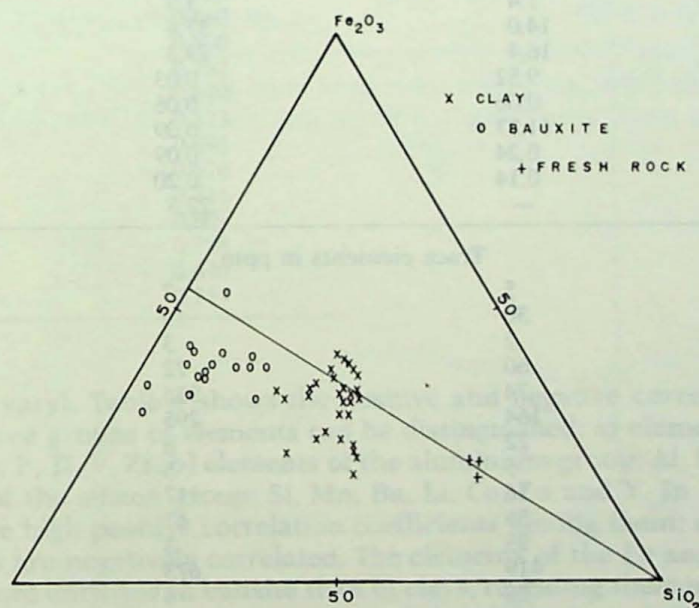Table 1. *Distribution of samples in each pit*

PIT	DEPTH (m)	TOPOGRAPHIC POSITION	NUMBER OF SAMPLES
A	8.3	top	9
B	2.0	upper slope	6
C	3.5	slope	10
D	8.9	slope	12
E	5.0	slope	7

The major and trace elements (Al, B, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, P, Pb, Si, Sn, Sr, Ti, V, Y, Zn and Zr) were determined by ICP for fifty samples. Loss on ignition was estimated by difference. Samples from pits A, B, and C, and the three samples of fresh rock summing up 28, were analysed for rare earth elements by ICP.

RESULTS

Classification of the samples

According to their contents in Al_2O_3, Fe_2O_3 and SiO_2, the samples were plotted in a triangular diagram (Fig. 2). Bauxites are considered here samples which contents in Al_2O_3 are greater than 30 % and contents in SiO_2 are less than 16 %. Otherwise they are called clays. The lateritization of the amphibolites forming clays and bau-

Fig. 2. Samples plotted in $SiO_2 - Al_2O_3 - Fe_2O_3$ diagram

xites is characterized by a strong loss of silica. The ratio Fe_2O_3/Al_2O_3 is generally greater in fresh rock than in clays and bauxites, thus indicating that iron is depleted in relation to aluminum during weathering.

Behavior of major and trace elements

The average composition for fresh rock and its weathering products is shown in Table 2. Lateritic products have much higher contents in Fe, Al, Ti, LOI, Cr, Pb, V and Zr, and lower contents in Si, Mn, Li, Y and Zn than fresh rock; they are totally depleted in Ca, Mg and Sr.

Isovolumetric calculations for major element (Table 3) show that in bauxites Ca and Mg are totally leached, Si is almost totally leached, Fe is slightly leached and Al remains nearly constant. In clays the tendencies are the same, the loss of silica being less intense. Such calculations demonstrate that the observed Fe enrichment in bauxites and clays is relative, that is, iron is just less depleted than other elements (Si, Mg and Ca).

Pearson's correlation coefficients were calculated for 47 samples (weathering products) and 22 variables (Mo, K and Sr have been excluded because their con-

Table 2. *Average contents in major and trace elements for 50 samples*

	FRESH ROCK n = 3	BAUXITE n = 17	CLAY n = 30
Major elements in % weight			
SiO_2	48,8	8,1	27,0
TiO_2	1,4	1,9	1,7
Al_2O_3	14,0	37,4	27,1
Fe_2O_3	16,4	29,3	25,6
CaO	9,52	0,03	0,03
K_2O	0,06	0,06	0,07
MgO	11,77	0,09	0,08
MnO_2	0,24	0,09	0,24
P_2O_5	0,14	0,20	0,12
LOI	—	22,8	18,0
Trace elements in ppm			
B	5	7	17
Ba	30	19	54
Be	2	3	3
Co	60	72	88
Cr	74	558	255
Cu	164	295	182
Li	22	8	14
Mo	5	5	5
Pb	56	117	88
Sn	56	67	63
Sr	95	3	3
V	419	673	532
Y	28	4	10
Zn	121	58	101
Zr	70	126	96

Table 3. *Isovolumetric geochemical balance (% of gains and losses)*

SAMPLE	Si	Al	Fe	Ca	Mg	DENSITY
Clay	−85	−9	−37	−100	−100	1.2
Bauxite	−94	j0	−20	−100	−100	1.1
Bauxite	−94	+17	−28	−100	−99	1.3.
Bauxite	−94	+7	−36	−100	−99	1.2
Fresh Rock g/100 cc	66,82	22,82	36,45	18,87	20,35	3.01

Table 4. *Pearson's correlation coefficients > 0.5 (47 Samples, 22 Variables)*

Pairs of elements		Positive correlation coefficients	Pairs of elements		Negative correlation coefficients
Cr	Al	0,554	Ba	Al	0,528
Fe	Be	0,554	Mn	Al	0,545
Mg	Ca	0,675	Si	Al	0,811
Mn	Ba	0,552	Si	Cu	0,640
Mn	Co	0,714	Si	P	0,582
Mn	Li	0,561	Si	Pb	0,584
P	Be	0,602	Y	Al	0,547
P	Fe	0,606	Zn	Al	0,636
Pb	Al	0,606	LOI	Ba	0,559
Si	Ba	0,723	LOI	Mn	0,527
Si	Mn	0,611	LOI	Si	0,782
Ti	Be	0,757	LOI	Y	0,610
Ti	Fe	0,744			
Ti	P	0,538			
V	Be	0,903			
V	Fe	0,860			
V	P	0,590			
V	Ti	0,762			
Zn	Mn	0,610			
Zn	Si	0,573			
Zn	Y	0,695			
Zr	Be	0,676			
Zr	Fe	0,716			
Zr	P	0,805			
Zr	Ti	0,738			
Zr	V	0,640			
LOI	Al	0,719			

tents do not vary). Table 4 shows the positive and negative correlations greater than 0.50. Three groups of elements can be distinguished: a) elements of the iron group: Fe, Be, P, Ti, V, Zr; b) elements of the aluminium group: Al, LOI, Pb and Cr; c) elements of the silicon group: Si, Mn, Ba, Li, Co, Zn and Y. In each group the elements have high positive correlation coefficients among them; elements of different groups are negatively correlated. The elements of the Fe and Al groups are in average more enriched in bauxite than in clays, revealing their marked residual behavior during weathering. The elements of the Si group are in average depleted in lateritic product as a consequence of their high solubility. However, except for
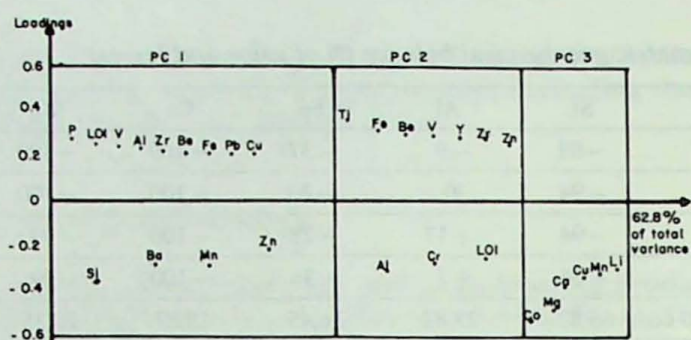
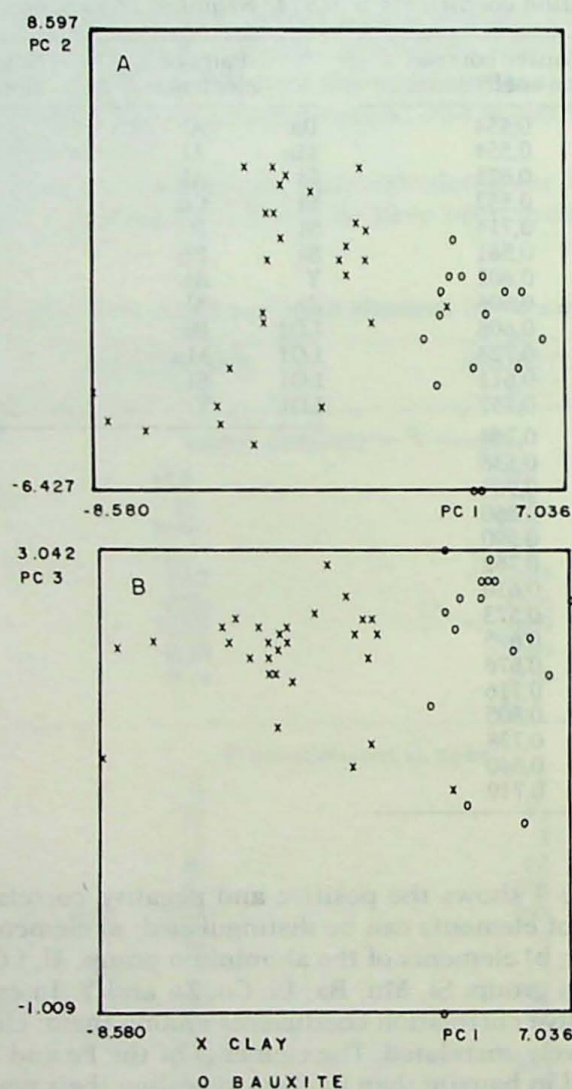Fig. 3. Loadings for the three first principal components

Fig. 4. **A.** Plot of PC1 × PC2 — obtained by PCA analysis of the whole set, **B.** Plot of
PC1 × PC3 — obtained by PCA analysis of the whole set

Si, they can be eventually enriched in some samples of clays and bauxites, more often in the first than in the latter.

Principal component analysis (R-mode) has been made for 47 samples and 22 variables. Three principal components account for 62,8 % of the total variance. Their main loading factors are displayed in Fig. 3, where the components are represented by rectangles whose widths are proportional to the fractions of the total variance explained. Only absolute values of the loadings superior to 0.20 have been included. The first PC is a linear combination with positive coefficients for elements of residual behavior (iron and aluminium group) and negative coefficients for more soluble elements. This PC explains 31.1% of the total variance. The second PC (20.4 % of the total variance) is dominated by elements of the iron group with high positive loadings, and the elements of the aluminum group with high negative loadings. PC 3 (11.3 % of the total variance) is dominated by the more soluble elements. The rest of the PC's are more difficult to interpret and upon preliminary inspection do not reveal significance in terms of geochemical processes. Fig. 4 is a scatter diagram of scores for PC1 × PC2 and PC1 × PC3; the samples of clay and bauxite are shown by different symbols. PC1, representing the elements of residual behavior, makes very well the distinction between bauxites and clays. Because bauxites concentrate as well the elements of the aluminum group as the elements of the iron group, they are not distinguished from clays by PC2 (Fig. 4A). PC 3 presents high negative loading values for Co, Mg, Ca, Cu, Mn and Li, that is, samples with high contents in such elements will be plotted in the lower part of PC1 × PC3 diagram. PC3 values for bauxites range in a larger interval than for clays. Thus, although values of Mn, Co and Li are in average higher for clays than for bauxites, the samples which have the highest contents of these elements are bauxites, especially those of Pit B.

Behavior of the rare earth elements

REE contents in fresh rock have been normalized to chondrite. Figure 5 shows a flat pattern with REE abundances about ten times over those of chondrites. It's
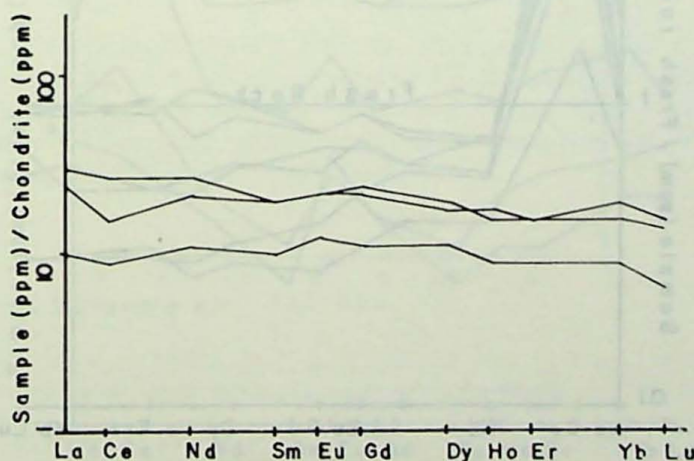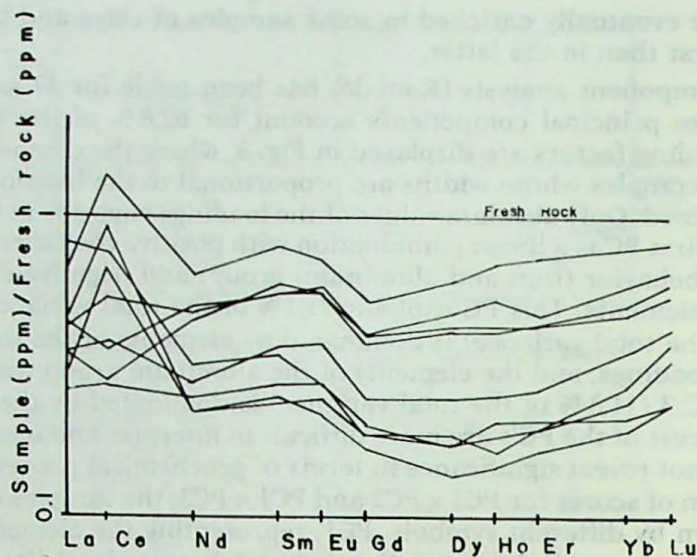

Fig. 5. REE pattern for fresh rock

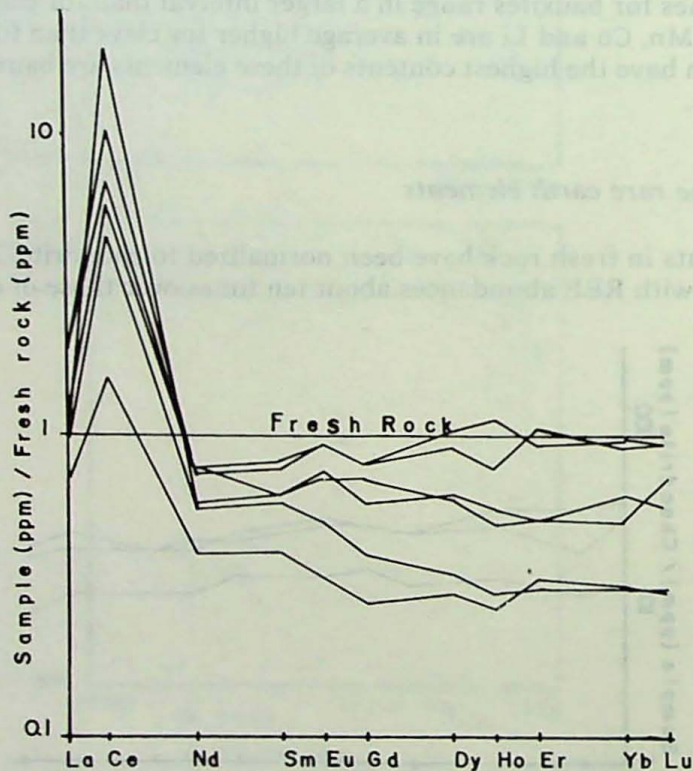Fig. 6. REE pattern for samples from pit A

Fig. 7. REE pattern for samples from pit B

typical of ocean floor tholeiitic basalts, from which the amphibolites seem to have been derived [3].

In order to investigate the REE fractionation during weathering, the REE contents of weathered products have been normalized to average values in fresh rock. Figures 6, 7 and 8 represent the REE pattern for samples from pits A, B and C, respectively.

In pit A the sum of REE contents in weathered product is less than in fresh rock (Table 5). Ce and La are less depleted than the other REE. Some samples present Ce positive anomalies. All the heavy REE are depleted, but they show a rising tendency according to the increasing atomic number (Fig. 6). In pit B, the sum of REE in weathered products is greater than in fresh rock (Table 5), but the only elements which are actually enriched are La and Ce, the latter showing very strong positive anomalies (Fig. 7). In pit C, the sum of REE in weathered products is slightly less than in fresh rock (Table 5). In this pit, 3 samples are untypical, being strongly depleted in REE. In general, La is somewhat depleted an Ce is enriched, showing positive anomalies. Eu, although depleted, shows also positive anomalies. The heavy REE show the same tendency as in pit A: the heavier are less depleted (Fig. 8).
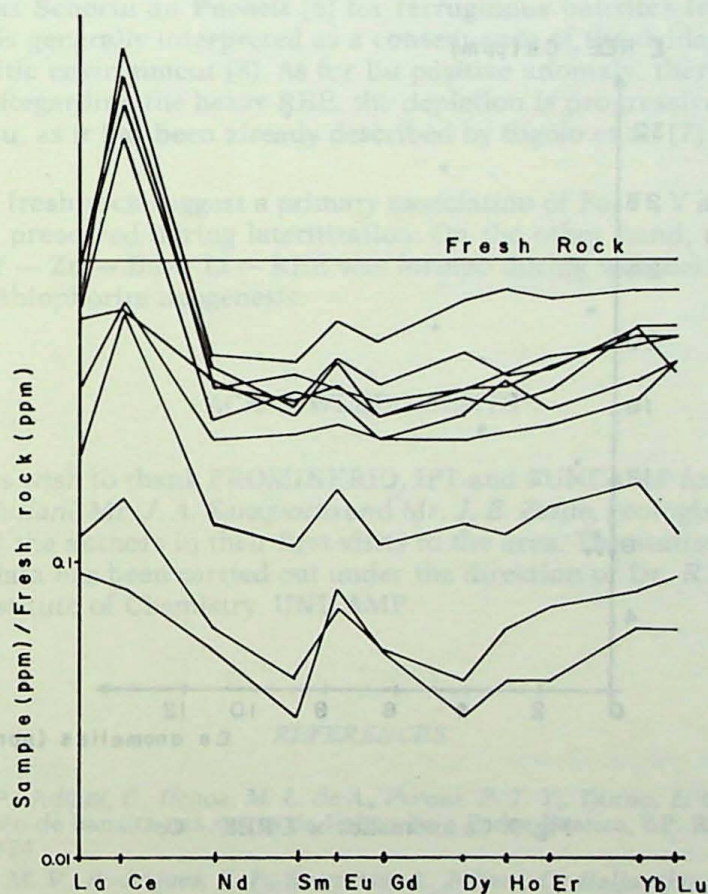

Fig. 8. REE pattern for samples from pit C

In all pits there are positive Ce anomalies which are stronger in more REE enriched samples (Fig. 9). REE have a general behavior during weathering similar to the elements of intermediate solubility — Mn, Co, Y — being generally depleted in bauxite and clays, but occuring locally in higher amounts (Table 5).

Table 5. *Average contents in Mn, Co, Y, Ce and Σ REE (ppm) for weathered products and fresh rock in pits A, B, and C*

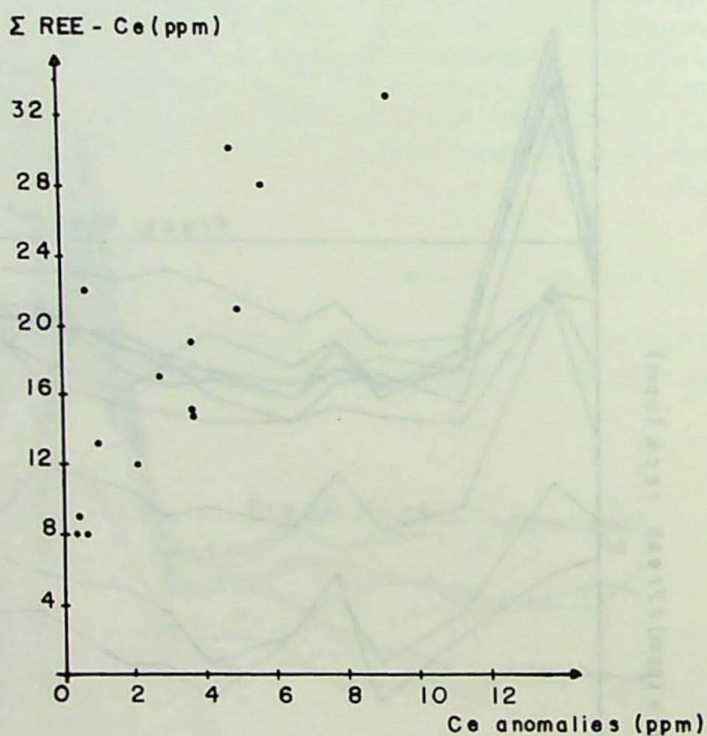| PITS	Mn	Co	Y	Ce	Σ REE
A	400	16	3	7	21
B	1300	195	10	91	115
C	1000	56	7	24	36
Fresh rock	1700	60	28	11	43

Fig. 9. Ce anomalies $\times$ Σ REE — Ce

CONCLUDING REMARKS

The lateritic weathering of the amphibolites of the Itaberaba Ridge led to the formation of an alteration blanket made up of iron rich bauxites on tops and upper slopes, and clay at the lower topographic levels, where the was less intense.

The elements of the Fe-group (Be, P, Ti, V, Zr) and the Al-group (LOI, Pb, Cr) are more concentrated in clays and bauxites than in fresh rock. Ca, Mg and Sr are totally leached from the weathering profiles. Mn, Co, Y, Zn, Ba and Li have during lateritization an intermediate behavior between the residual and the soluble elements. Although generally depleted in weathered products, they can be found concentrated in samples containing lithiophorite concretions.

Similar behavior for trace elements in iron-rich bauxites have been described by Lopes [5] for granulite derived bauxites from Miraí (Brazil).

REE presents strong fractionation during lateritization. Except for Ce, they are depleted in weathered products reaching higher values only in samples enriched in Mn. This correlation indicates that litiophorite concretions concentrate REE. Positive anomalies have been found for Ce and Eu. Sígolo et al. [7] have also found Ce positive anomalies in bauxites and related products from Passa Quatro (Brazil), as well as Schorin an Puchelt [6] for ferruginous bauxites from Venezuela. This feature is generally interpreted as a consequence of the oxidation of Ce^{3+} to Ce^{4+} in lateritic environment [8]. As for Eu positive anomaly, there is no evident explanation. Regarding the heavy REE, the depletion is progressively less intense from Gd to Lu, as it has been already described by Sígolo et al. [7] and Schorin & Puchelt [6].

Analysis of fresh rock suggest a primary association of Fe, Ti, V and REE which was partially preserved during lateritization. On the other hand, the association Mn — Co — Y — Zn — Ba — Li — REE was formed during weathering, corresponding to the lithiophorite neogenesis.

ACKNOWLEDGMENTS

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