

Control of the distribution of Mn, Co, Zn, Zr, Ti and REEs during the evolution of lateritic covers above ultramafic complexes

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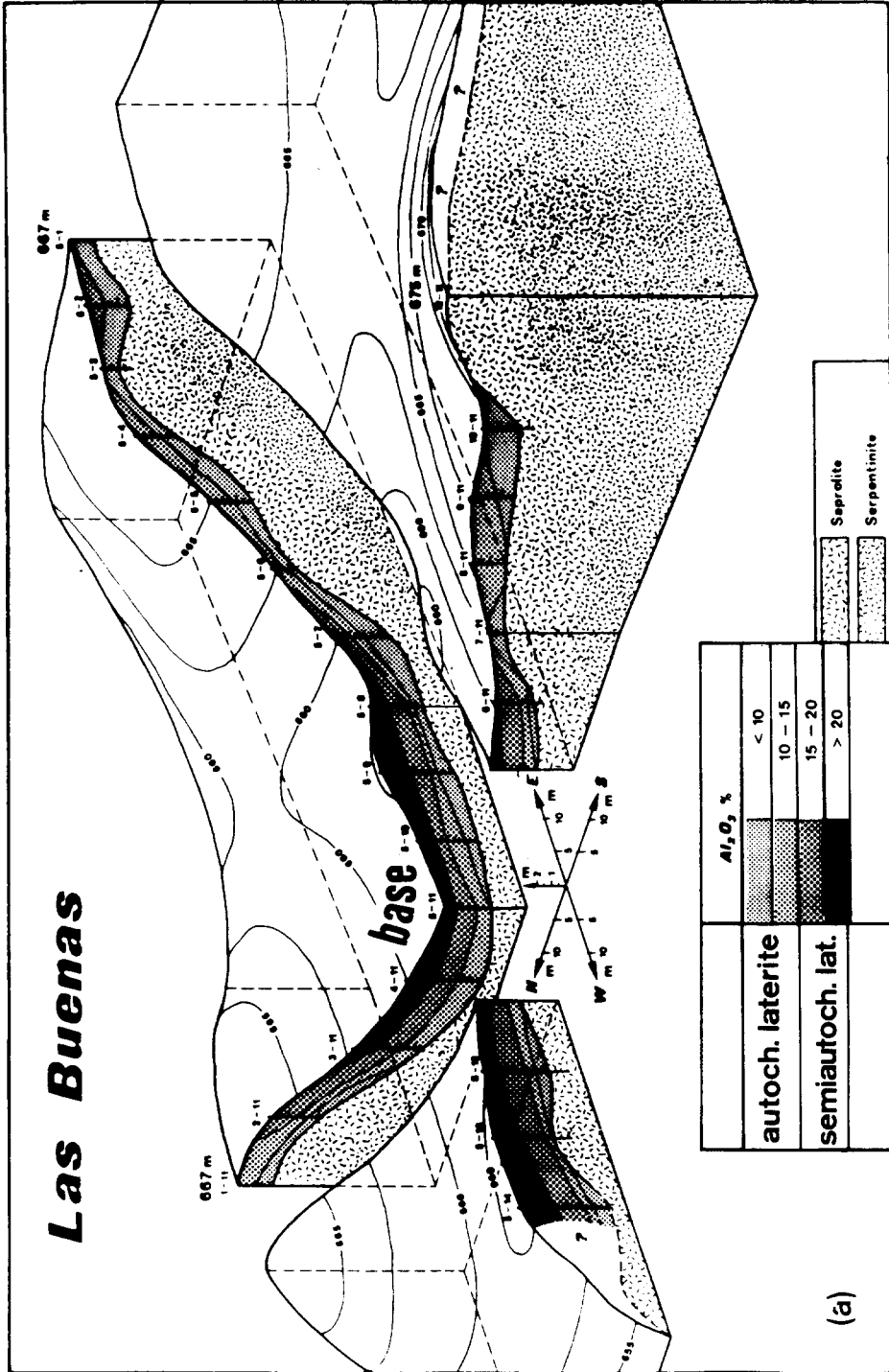
ABSTRACT

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Laterites above ultramafic complexes in Brazil and the Philippines consist of *in-situ* (autochthonous) and partly transported (semi-autochthonous) horizons. Enrichment and distribution of minor and trace elements in the laterites are controlled by weathering processes and the morphology of the peridotite massifs. Mn and Co migrate towards the base of doline-like depressions of the peridotite karst where they precipitate in the ferruginous horizon above the saprolite, due to rising pH and concentration of the solution. Mass balance calculations reveal absolute enrichment of Mn and Co and depletion of Zn and Cr. Semi-autochthonous laterites represent a mixture of Fe-Cr-rich limonitic material derived from ultramafic rocks and Al-Si-Ti-Zr-rich kaolinitic material derived from sialic rocks. They may reveal unusually high contents of Al₂O₃, SiO₂, TiO₂ and Zr, thus camouflaging the underlying ultramafic bedrock. During and after deposition of semi-autochthonous laterites, acidic leaching under humid (sub-) tropical climate leads to the mobilization of REEs from the weathering products of sialic rocks. Subsequent migration and precipitation of REEs together with Mn at the base of depressions result in concentrations of predominantly Ce which under favourable conditions exceed 0.5 wt.%. High proportions of sialic weathering material in laterites can be expected in geological settings where ultramafic and sialic rocks occur in close spatial association. Enrichment of REEs in weathering profiles above ultramafics is favoured by the abundance of weathering material from REE-rich alkaline rocks like those of the Alkaline Complex of Jacupiranga, Brazil.

INTRODUCTION

Anomalously high local concentrations of transported sialic Al-Si-Ti-Zr-rich material in laterite covers above ultramafic complexes have been reported by Trescases (1975), Golightly (1981) and Butt and Nickel (1981). Schell-



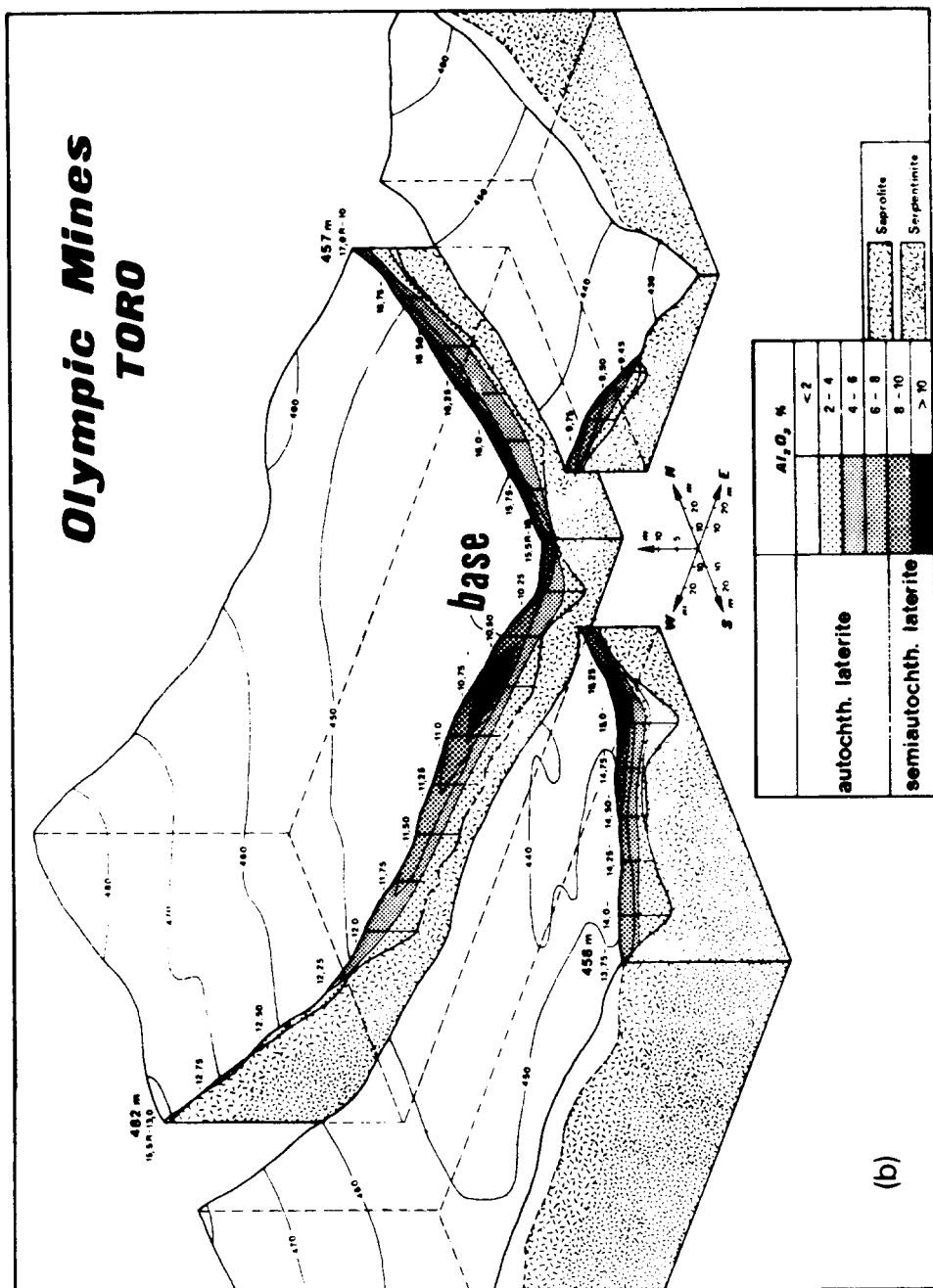


Fig. 1. Lateritic weathering profiles in depressions of the peridotite karst, featuring the Al_2O_3 content and the boundary between autochthonous and semi-autochthonous laterite.

mann (1989) emphasized the importance of mechanical transport for the evolution of the thick and extensive laterite covers above ultramafics in Burma. The processes leading to the formation of partly transported (semi-autochthonous) laterites are not thoroughly investigated yet. Friedrich et al. (1990) pointed out the significance of heavy minerals for the recognition of semi-autochthonous laterites.

In this study, some aspects regarding the characterization and evolution of laterites overlying ultramafic complexes with emphasis on semi-autochthonous laterites are presented. Special attention will be given to the role of morphology and bedrock composition on the distribution of certain trace elements in the laterites and implications for mapping and mineral prospecting in tropical areas. The application of heavy-mineral (HM) contents as an internal standard for mass balance calculations casts a new light on the mobility of trace elements in the supergene environments.

METHODS

Chromite exploration in seven areas of the Philippines and Brazil yielded data on the composition of lateritic weathering material (Friedrich et al., 1984, 1987a). Three of these areas (Las Buenas and Olympic, Philippines and Jacupiranga, Brazil) were selected for this paper. Depressions in the peridotite karst were studied along toposequences (Fig. 1). Sampling of laterite and bedrock was carried out using hand augers and motorized drills. Lateritic material was disintegrated in an attrition cell to < 1 mm and separated by hydrocycloning at $30 \mu\text{m}$. Since the grain size distribution of accessory chrome-spinels in ultramafics has its maximum between 70 and $200 \mu\text{m}$, the hydrocyclone coarse fraction $> 30 \mu\text{m}$, consisting almost totally of HMs, contains more than 95 wt.% of the total chrome-spinel content (Friedrich et al., 1984).

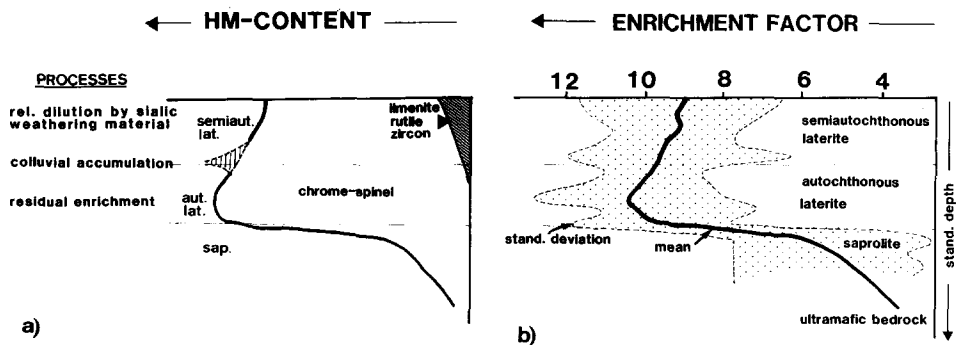


Fig. 2. (a) Distribution of heavy minerals (HM) and (b) their enrichment relative to bedrock in laterites overlying ultramafic complexes; mean is calculated from 27 profiles (225 samples) of Olympic/TORO, normalized to standard depth.

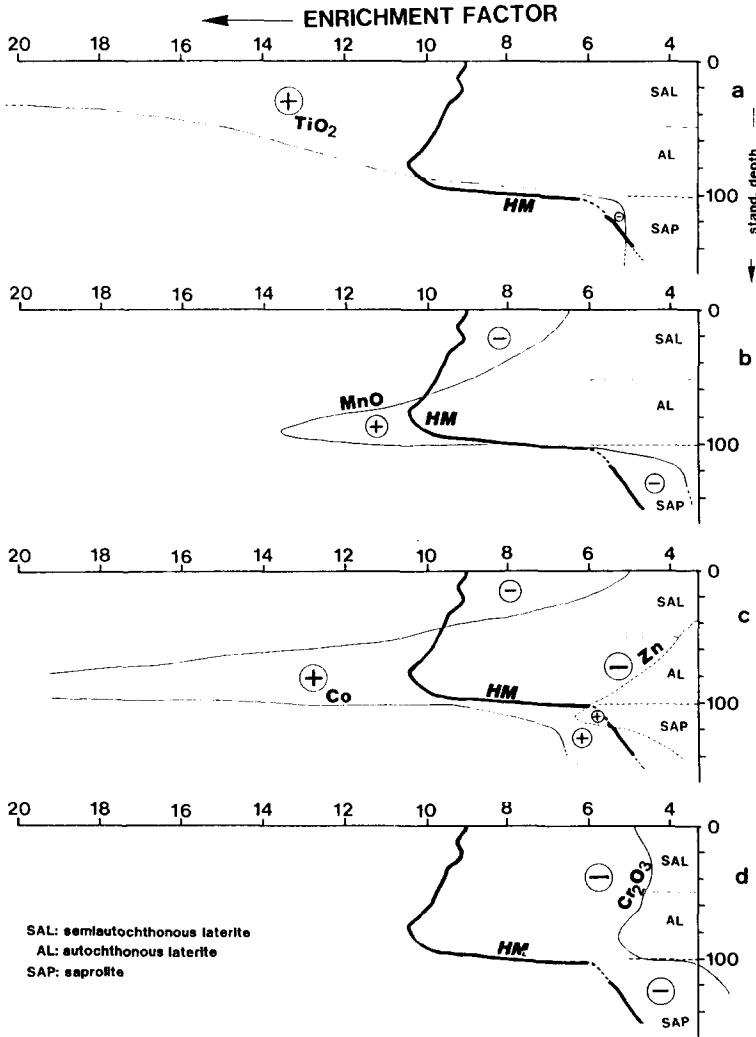
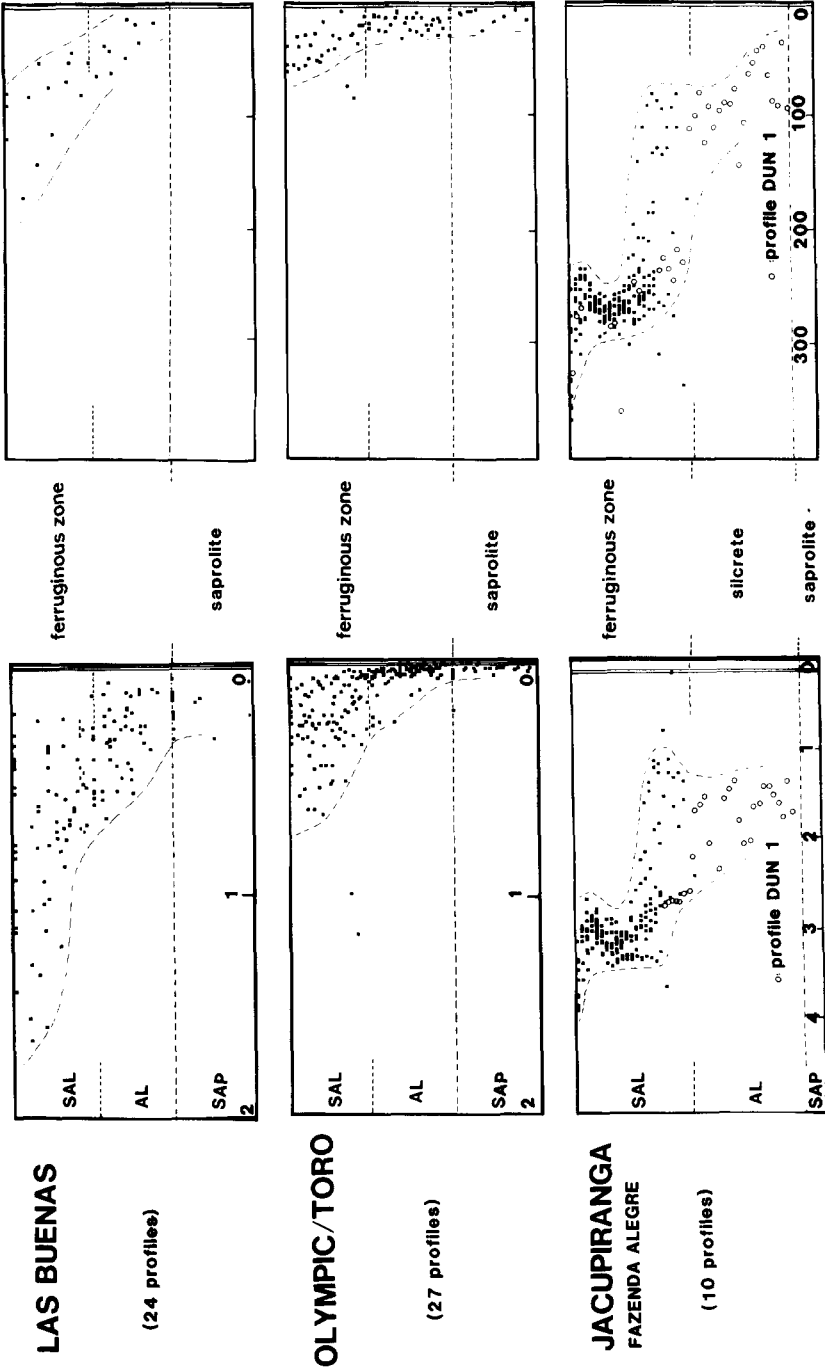


Fig. 3. (a-d) Mass balance of minor and trace elements in laterites (fraction $< 30 \mu m$) overlying ultramafic complexes, featuring absolute enrichment (+) and depletion (-) of the elements relative to the HM content as an internal standard; curves of HM and element distributions are calculated from 27 profiles of Olympic, Philippines.

This fraction was progressively separated by Mozley shaking table and magnetic separators in order to eliminate magnetite, silicates and limonite aggregates. The final concentrate contains chrome-spinel and minor amounts ($\ll 5$ wt.%) of ilmenite, Ti magnetite and zircon. Microscopic and microprobe analyses were carried out to determine the alteration state of the heavy minerals and their chemical composition. Since the chrome-spinels in *in-situ* laterites of Las Buenas and Olympic were essentially unweathered, their con-



SAL: semiautochthonous laterite
 AL: autochthonous laterite
 SAP: saprolite

Fig. 4. Distribution of TiO₂ and Zr in laterites (fraction < 30 μm) of peridotite karst depressions in the Philippines and Brazil; double vertical lines indicate contents of the element in the ultramafic bedrock; profile DUN 1: drillhole down to saprolite.

tents (wt.%) were used as internal standard for mass balances of the lateritic weathering (Friedrich et al., 1987b). For this purpose, chrome-spinels of the ultramafic bedrock were separated by selective crushing and grinding of 1–2 kg of rock material and subsequently concentrated by Mozley table, bromoform and magnetic separation. The chrome-spinel composition was determined by microprobe, while the Cr_2O_3 content of the HM-free silicate matrix was analyzed by XRF in order to differentiate between Cr bound to chrome-spinel and Cr bound to silicates. Mass balances were calculated by comparing the enrichment of chrome-spinel contents in the laterite relative to bedrock (Fig. 2b) to the enrichment of MnO, TiO_2 , Cr_2O_3 , Co and Zn of the lateritic fine fraction $< 30 \mu\text{m}$ relative to bedrock, as shown in Figure 3a–d. For Cr_2O_3 , mass balance was carried out by comparing the chrome-spinel-free silicate fraction of the bedrock to the Cr_2O_3 content of the lateritic fine fraction, which contains $\ll 3$ wt.% of the total chrome-spinel content. Lateritic fine fraction $< 30 \mu\text{m}$ and bulk laterites were analysed by XRF for minor and trace elements. REE analyses were carried out by neutron activation and ICP.

In Figures 2–7, profiles of different depth from one area are normalized to standard depth. Thus the results from different profiles can be shown in a single diagram for direct comparison. The standard depth was calculated according to the following formula:

$$\text{Stand. depth} = \frac{(\text{actual depth (cm)} - 50) \times 100}{(\text{saprolite depth (cm)} - 50)}$$

The saprolite depth of the profile is defined as the boundary between the saprolite and the ferruginous zone. The profile then is normalized to this depth, which always corresponds to a standard depth value of 100. Since samples were taken along intervals of 50 cm, this value has to be subtracted in order to achieve standard depth 0. The ferruginous zone is characterized by almost total depletion of alkalis and alkaline earths, having an MgO content of < 2 wt.%.

THE STUDY AREAS

Serpentinized dunites of the Las Buenas Mine in Mindanao and serpentinized harzburgites of Olympic Mines/TORO in Palawan form part of Cretaceous ophiolite sequences in the Philippines. The average chemical composition of the ultramafics shows low concentrations of incompatible elements like Ce and Zr, typical for ultramafic rocks of ophiolitic affiliation (Table 1).

In the vicinity of the dunites of Las Buenas, reef limestone and quartz diorite occur. In the Olympic Mines, harzburgites are associated with microgabbros and troctolites. Gabbros, basalts, spilites, plagiogranites and sedimen-

TABLE 1

Average chemical composition of ultramafic rocks from the Philippines and Brazil (XRF analyses in wt.%, ppm); data from Friedrich et al. (1984, 1987a)

	LB — Las Buenas Mine Mindanao/ Philipp.; serpentinized dunite	TORO — Olympic Mines Palawan/Philipp.; serpentinized harzburgite	JAC — Fazenda Alegre Jacupiranga/Brazil; serpentinized dunite
\bar{x} (wt.%)			
SiO ₂	38.1 ± 2.68	40.5 ± 1.82	38.7 ± 1.03
Al ₂ O ₃	0.66 ± 0.33	1.21 ± 1.98	0.26 ± 0.12
Fe ₂ O ₃	9.00 ± 2.08	8.56 ± 1.00	12.55 ± 0.16
MgO	35.7 ± 0.33	36.3 ± 1.94	37.4 ± 1.63
Na ₂ O	0.46 ± 0.73	<0.1	<0.1
K ₂ O	<0.02	<0.02	<0.02
CaO	<0.02	0.024 ± 0.02	0.23 ± 0.17
LOI	15.5 ± 0.8	13.42 ± 1.31	9.23 ± 0.77
Total	99.40	99.94	98.35
\bar{x} (ppm)			
MnO	1000 ± 100	1100 ± 100	2000 ± 100
Co	160 ± 31	85 ± 20	190 ± 43
TiO ₂	180 ± 8	100	1100 ± 400
V ₂ O ₃	60 ± 5	66 ± 6	60 ± 3
Cr ₂ O ₃	6000 ± 3800	3500 ± 770	10870 ± 5400
Zn	53 ± 11	42 ± 8	85 ± 9
Ce	<10	<10	81 ± 16
Zr	<20	<20	<20
<i>n</i>	23	10	3

tary rocks occur in topographically elevated areas proximal to the harzburgites (Rammelmair et al., 1987).

The Alkaline Complex of Jacupiranga/Brazil consists of a body of highly serpentinized dunite, associated with alkali-pyroxenites (jacupirangite) and nephelinic pyroxenites and syenoids (melteigite and ijolite), peralkaline rocks and carbonatites. A fenitization zone is developed at the contact of the complex with the sialic basement rocks. As a result of the intrusion of nepheline-pegmatitic and syenitic veins in the dunite, the contents of incompatible elements like Ce are locally elevated and inhomogeneously distributed (Germann et al., 1987; Table 1).

The recent climatic conditions in the Philippine areas are humid tropical with annual precipitation rates between 2500 and 3000 mm, while Jacupiranga is characterized by precipitation of 1500 to 1700 mm/a. In all areas, a dense tropical rainforest vegetation persisted until a few decades ago. The

formation of peridotite karst has developed as a result of intensive leaching during the weathering of the ultramafics. Slope angles between 10 and 20° are common. Swamps in topographic depressions of the karst landscape indicate temporarily restricted drainage.

THE LATERITE COVERS — RESULTS AND DISCUSSION

Semi-autochthonous horizons constitute the topmost portion of the weathering covers overlying the ultramafic complexes. They correspond to the “terres rouges” of New Caledonia (Trescases, 1975), the “transported limonites” of Golightly (1981), the “transported overburden” of Butt and Nickel (1981) and the “allochthonous surface layers” of Schellmann (1989). Their geochemical and mineralogical features indicate that they consist of a mixture of autochthonous Fe-Cr-rich ferruginous material and transported Al-Si-Ti-Zr-rich kaolinitic material. Their thickness considerably increases from the slopes towards the base of the depressions of the peridotite karst (Fig. 1). They are of reddish-brown colour (2.5 YR 4/6–5YR 4/6, 5/6), having a loose homogeneous consistency without visible sedimentary structures and are characterized by abundant goethite, kaolinite, quartz and gibbsite with subordinate serpentine and chlorite. Within this horizon, the proportions of HM species like zircon, ilmenite, Ti magnetite and rutile, primarily absent in the underlying ultramafics, increase upward while the proportions of “ultramafic” chrome-spinels decrease, being indicative for the partly transported origin of this profile portion (Friedrich et al., 1990; Fig. 2a). In Las Buenas and Olympic, the semi-autochthonous laterite is underlain by a horizon of yellowish-brown colour (5 YR 5/6–7.5 YR 4/4, 5/6) with relic fabrics in its lower portion, consisting mainly of goethite and some secondary quartz. The HM assemblage consists exclusively of chrome-spinel and fine-grained magnetite, derived from the ultramafic parent rock. In Jacupiranga, the semi-autochthonous laterite is underlain by a silcrete zone with ferruginous portions, showing relic structures of the ultramafic bedrock and nepheline-pegmatitic veins which intersect the ultramafics. This zone is considered to coincide with the erosion level of a former landscape on which the semi-autochthonous laterite has evolved (Oliveira and Trescases, 1985). Relic structures of the parent rock and HM assemblages indicate that the profile zone underneath the semi-autochthonous laterite represents the *in-situ* weathering product of the ultramafic bedrock, thus being referred to as autochthonous laterite (Friedrich et al., 1990). There is a gradational change to saprolite with depth, which in Jacupiranga consists predominantly of chlorite/vermiculite mixed layer minerals and in Las Buenas and Olympic of serpentine.

Geochemical evolution of the weathering cover

The trace-element distribution of the laterites is controlled by (1) autochthonous weathering processes, (2) the formation parameters of the semi-autochthonous laterite and (3) acidic leaching of this profile zone. Regarding the composition of laterites above ultramafics, elements which predominantly form weathering resistant HMS like chrome-spinel (Cr), ilmenite and rutile (Ti) or zircon (Zr) can be distinguished from elements like Mn, Co, Ni, Cr and Zn which are released during weathering from relatively unstable minerals like olivine, pyroxene or serpentine.

Upper saprolite and autochthonous laterite

These zones generally are characterized by oxidizing conditions and slightly alkaline pH, becoming more acid towards the profile top under the influence of percolating surface waters (Trescases, 1975; Golightly, 1981). In Olympic, a pH of 8 was measured in the upper saprolite decreasing to pH 3 near the surface (Friedrich et al., 1984). In Las Buenas and Olympic, depletion of alkalis, alkaline earths and mobilization of most of the silica indicate good drainage conditions during profile evolution. Here the ferruginous *in-situ* profile consists of goethite and subordinate secondary silica (Friedrich et al., 1984). In Jacupiranga, the occurrence of smectite and chlorite-vermiculite besides goethite and secondary silica indicates restricted drainage during profile evolution (Oliveira and Trescases, 1985).

Due to depletion of alkalis and silica, the weathering-resistant chrome-spinels become residually enriched by factors of 4–6 in the upper saprolite (Fig. 2b). During initial weathering in the saprolite, Ti remains essentially stable relative to the HMS as internal standard (Fig. 3a). In groundwaters between pH 5 and 9, the solubility of Ti is almost zero (Cramer and Nesbitt, 1983). In the upper part of the autochthonous laterite, the significant enrichment of Ti is probably due to leaching of clay minerals and fine-grained ilmenite and leucoxene from the semi-autochthonous laterite, as also reported by Schellmann (1989) for laterites above ultramafic rocks.

That part of the Cr which is bound to the silicate minerals of the ultramafics, in contrast to the Cr of chrome-spinels, becomes absolutely depleted in the upper saprolite (Fig. 3d). Part of this Cr may be leached downward in the form of $\text{Cr}(\text{OH})_3$ hydrosols in alkaline and oxidizing environments (Seeliger, 1961). Indications of this process can be observed in Jacupiranga, where newly formed Cr-bearing phyllosilicates have developed in deeper zones of the saprolite. In the ferruginous zone, the remaining Cr becomes fixed in goethite (Schellmann, 1978). Towards the top of this zone, no significant absolute enrichment or depletion of Cr is observed (Fig. 3d). In the harzburgites of Olympic Mines, about 65 wt.% of the total Cr content of the ultramafics is bound in silicates and less than 35 wt.% in chrome-spinels (Table 2). Conse-

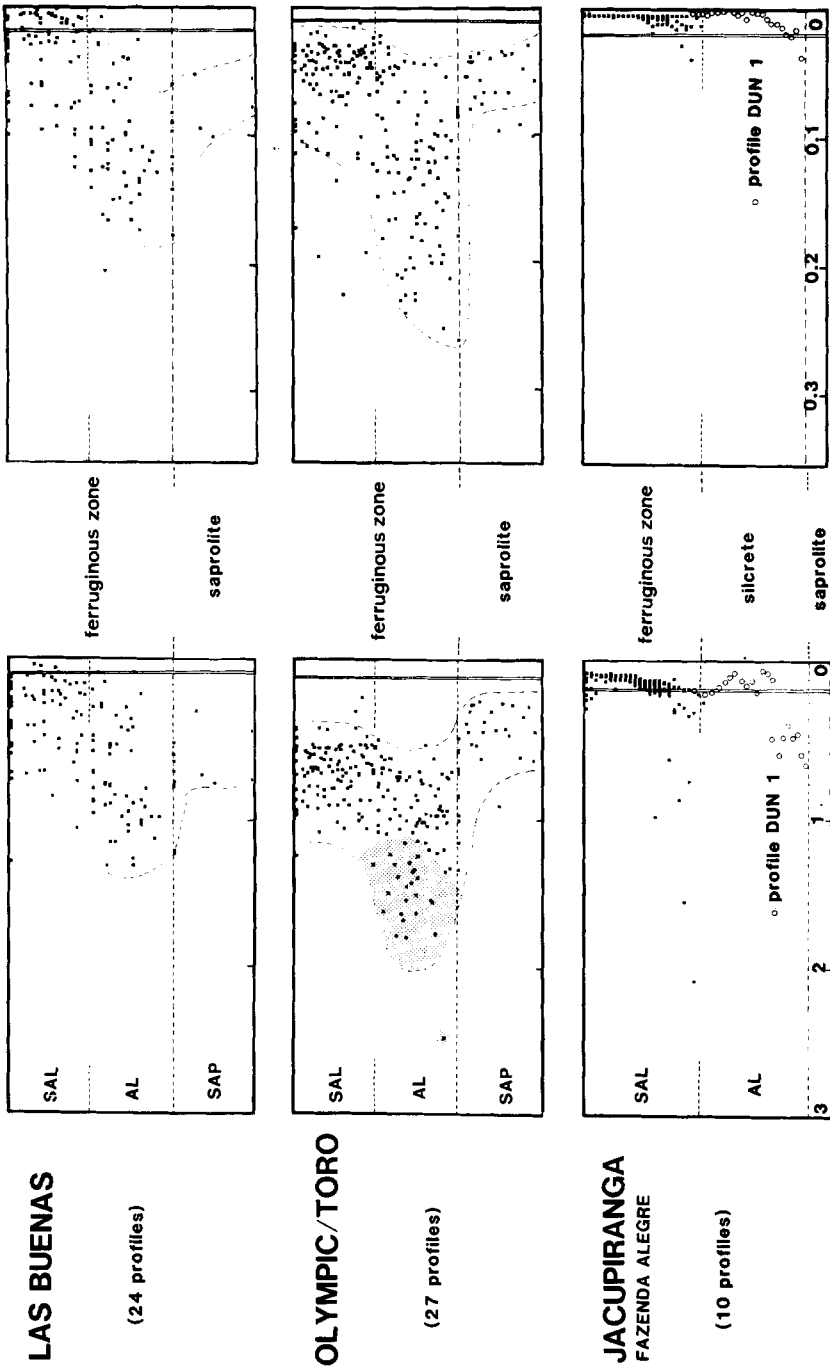
TABLE 2

Proportions and Cr₂O₃ content (wt.%) of silicates (SIL), magnetite (MAG) and chrome-spinel (CHR) of harzburgites from Olympic, Philippines (after Jochum, 1988)

	Sample OR 241			Sample OR 242			Mean		
	SIL	MAG	CHR	SIL	MAG	CHR	SIL	MAG	CHR
Proportion of mineral phase in harzburgite	99.4	0.22	0.33	99.3	0.38	0.29	99.4	0.30	0.31
Cr ₂ O ₃ content of mineral phase	0.33	0.66	51.0	0.25	0.19	51.0	0.29	0.43	51.0
Cr ₂ O ₃ content of mineral phase relative to bulk rock	0.33	0.001	0.17	0.25	0.001	0.15	0.29	0.001	0.16
Total Cr ₂ O ₃ content of all phase relative to bulk rock		0.4953			0.400			0.448	
Proportional percentage on the total Cr ₂ O ₃ content	65.7	0.3	34.0	63.9	0.18	36.9	64.4	0.25	35.3

quently, the total Cr content of laterites above ultramafics has to be subdivided into an essentially immobile portion, bound to chrome-spinels, and a soluble part, bound to silicates. Thus, the bulk Cr content of laterites may not serve as an internal standard for mass balances under the conditions discussed above.

As already shown by Golightly (1979), Mn is partly mobilized and removed in its divalent form in the zone of waterlogging of the deeper saprolite (Fig. 3b). For this reason, its strong enrichment in the lower ferruginous zone is only explained by significant vertical and/or lateral supply. Vertical supply may be due to leaching of Mn from the near-surface parts of the profile. Mobilization of Mn from surficial profile zones is possible under conditions of low pH and high CO₂ activity which can be provided by a dense vegetational cover (Jenne, 1968; Eichler, 1970). Tropical rainforest vegetation has persisted in the areas of investigation until recently. This environment even favours the reduction of Mn⁴⁺ to Mn²⁺ (Beauvais et al., 1987). Colloidal Mn⁴⁺ complexes are highly mobile and can be transported in form of sols over wide distances (Krauskopf, 1979). When Mn-bearing solutions reach the lower parts of the ferruginous zone, rising pH due to silicate hydrolysis and increasing concentration of the solution above the saprolite are likely to result in the oxidation of Mn²⁺ (Jenne, 1968) and/or precipitation of Mn oxides from colloidal solutions (Eichler, 1970). This process is enhanced by the catalytic action of already existing hydroxides (Schellmann, 1966; Jenne, 1968; Eichler, 1970; Trescases, 1975; Smith, 1977; Golightly, 1979; Crerar et al., 1980; Ogura et al., 1983).



SAL: semiautochthonous laterite
 AL: autochthonous laterite
 SAP: saprolite

Fig. 5. Distribution of MnO and Co in laterites (fraction <math> < 30 \mu\text{m}</math>) of peridotite karst depressions in the Philippines and Brazil, double vertical lines indicate contents of the element in the ultramafic bedrock; shaded areas comprise samples from the base of the depression; profile DUN 1: drillhole down to saprolite.

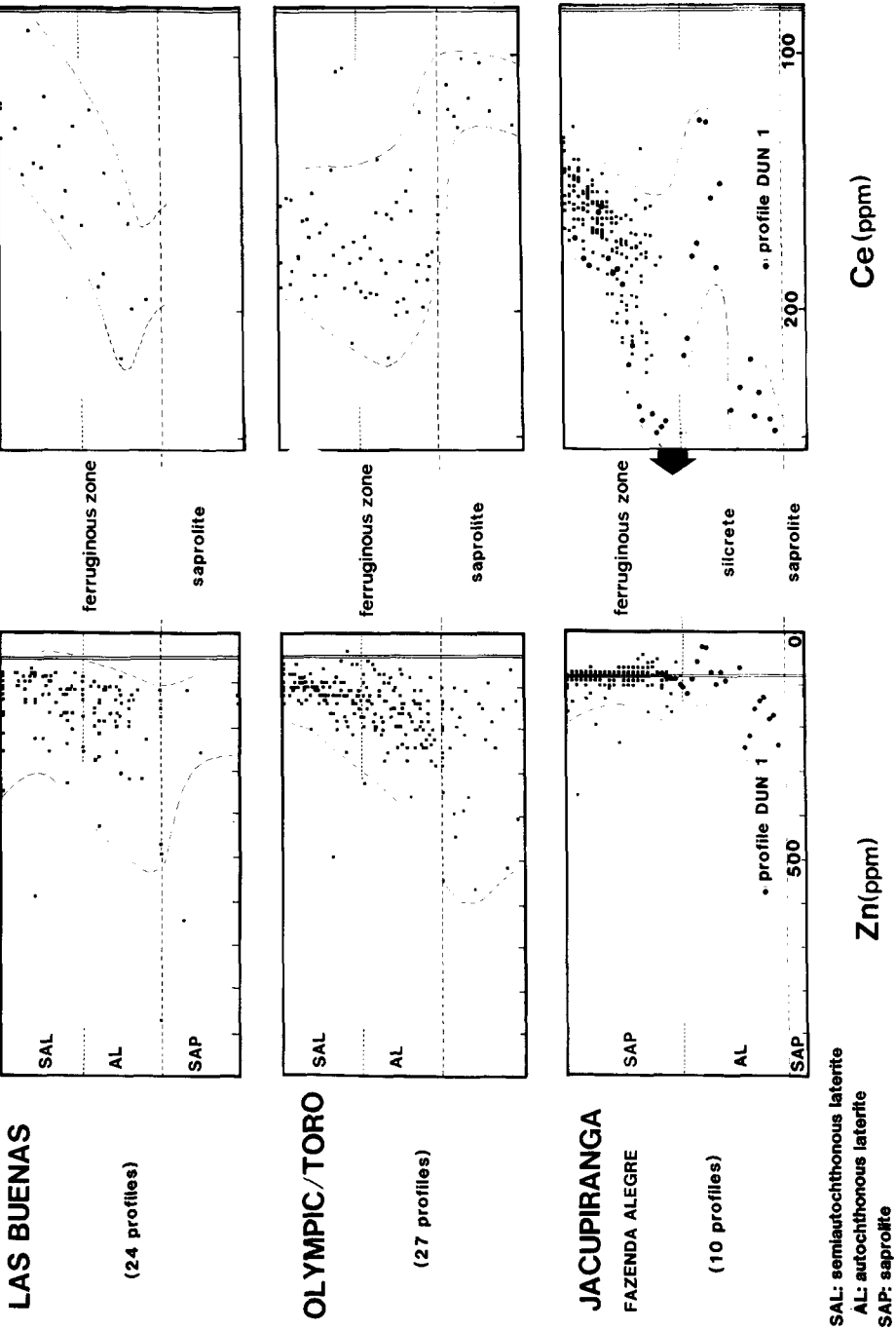


Fig. 6. Distribution of Zn and Ce in laterites (fraction <math>< 30 \mu\text{m}</math>) of peridotite karst depressions in the Philippines and Brazil; double vertical lines indicate the content of the element in the ultramafic bedrock; arrow indicates high Ce concentration in samples from the base of the depression; profile DUN 1: drillhole down to saprolite.

Cobalt is enriched in the upper saprolite where Ni silicates are abundant (Swaine and Mitchell, 1960; Hotz, 1964; Trescases, 1975). Since the enrichment of Co in the upper saprolite can only be observed in connection with abundance of Ni silicates as at Olympic, it can be assumed that these minerals scavenge Co from downward-migrating solutions. The distribution of Co is controlled by the same physico-chemical parameters as Mn (Fig. 5). It is initially adsorbed by negatively charged Mn^{4+} colloids and later incorporated into Mn oxides (Burns, 1976). Its precipitation at rising pH, however, is more effective, because the solubility product of its hydroxide is lower than for Mn (Trescases, 1975; Golightly, 1981). For this reason, the enrichment of Co in the lower ferruginous horizon exceeds the enrichment of Mn by a factor of 2 with Co being bound to Mn-oxides (Fig. 3c). Jenne (1968) establishes a critical pH of 6 for the initial precipitation of Mn and the formation of mostly non-stoichiometric Mn oxides like asbolite, lithiophorite, todorokite and cryptomelane. These minerals have vacant sites along $\langle MnO_6 \rangle$ octahedral layers, which can be occupied preferentially by cations like Co, Ni, Zn (Loganathan and Burau, 1973; Burns, 1976).

The mass balance of Zn indicates higher mobility and depletion in the lower ferruginous zone compared to Mn and Co (Fig. 3c). Slight enrichment of Zn in the saprolite may have resulted from scavenging by Ni silicates, as described also by Trescases (1975) and Schorin (1983). In general, the distribution trend of Zn is similar to that of Mn with the highest concentrations in the lower ferruginous zone (Fig. 6).

Semi-autochthonous laterite

In the semi-autochthonous laterite, the mass balance of Ti indicates enrichment factors of 10 to 70 relative to bedrock (Fig. 3a). Zr shows concentrations $\gg 20$ ppm, increasing towards the profile top (Fig. 4). Ti is mainly present as ilmenite, leucoxene and rutile while Zr is present as zircon. The abundance of these heavy minerals relative to the chrome-spinels increases towards the top of the semi-autochthonous laterite and is demonstrated by the high TiO_2 contents of the HM concentrates especially at the base of the karst depressions (Fig. 7). Furthermore, this horizon is characterized by high concentrations of Al and Si with Al_2O_3 reaching up to 30 wt.% (Fig. 1). Consequently, the contents of "ultramafic" elements like Mn, Co, Zn and Cr are low. A gradual increase of the Al, Si, Ti and Zr contents towards the top is characteristic for the semi-autochthonous horizon (Friedrich et al., 1990). The compositional distinction between autochthonous and semi-autochthonous laterite is demonstrated by the Ti-Al correlation (Fig. 8). The semi-autochthonous laterite has significantly higher contents of Al_2O_3 and TiO_2 and the increase in slope of the regression curve results from increasing proportions of Ti, present in HMS like ilmenite. High Al_2O_3 contents in autoch-

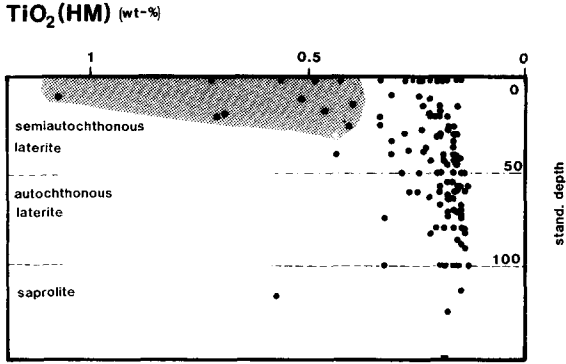


Fig. 7. Distribution of the TiO_2 contents of heavy mineral concentrates (HM) in lateritic weathering products of Las Buenas, Philippines. The diagram comprises all samples from 24 profiles of the area. The shaded area marks samples of the semi-autochthonous laterite from the base of the depression.

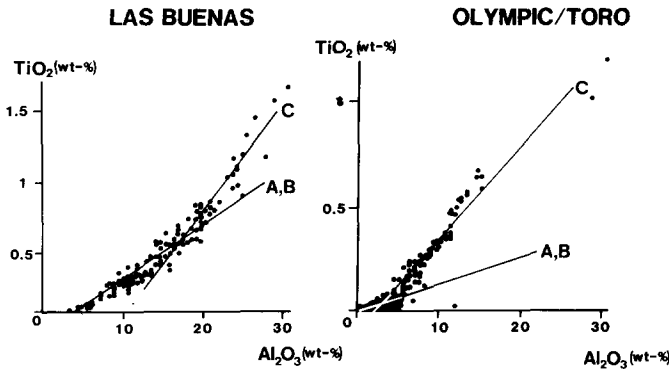


Fig. 8. Plot of the TiO_2 contents versus the Al_2O_3 contents of lateritic weathering material (fraction $< 30 \mu m$); A, B=saprolite and autochthonous laterite; C=semi-autochthonous laterite.

thonous laterites of Las Buenas result from illuviation of kaolinite from the semi-autochthonous laterite, especially at the base of karst depressions.

The high Ce contents in the laterites of Las Buenas and Olympic (Fig. 6) can only be explained by absolute supply of this element during profile evolution, since the dunites and harzburgites of Las Buenas and Olympic have Ce contents $\ll 10$ ppm (Table 1). It can be assumed that Ce is initially bound to weathering products of sialic rocks, which occur in close vicinity to the ultramafics. The subsequent acidic leaching of the upper semi-autochthonous laterites results in concentration of Ce in the lower ferruginous zone of the autochthonous laterite. Elevated concentrations of > 100 ppm Ce are found even in the saprolite (Fig. 6).

In Jacupiranga, Ce shows a concentration peak of > 5000 ppm in a zone of 1 m thickness at the bottom part of the semi-autochthonous laterite just above

TABLE 3

Rare earth element contents (ppm) of Mn-Fe concretions and alkaline rocks of the Jacupiranga Alkaline Complex, Brazil (neutron activation analyses)

	La	Ce	Nd	Sm	Eu	Yb	Lu
Mn-Fe concretion JL 1076	153	162000	–	45	12	16	1.2
Alkaline rocks							
JR 6014	30	59	29	6.3	1.7	1.2	0.2
JR 6064	8	–	–	4.3	1.2	0.8	0.1
JR 1111	38	71	33	6.7	1.8	1.0	0.1
JR 1113	9	18	–	2.1	0.7	–	0.1

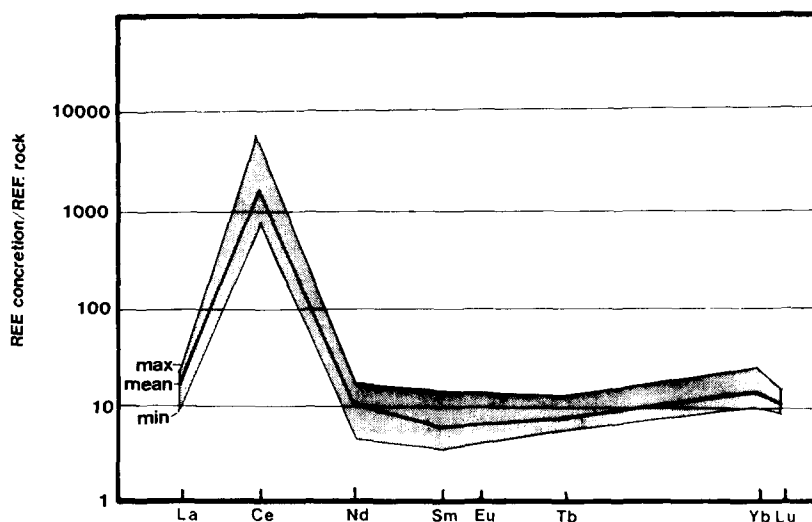


Fig. 9. Enrichment of Rare Earth Elements in Mn-Fe concretions from laterite profiles of Fazenda Alegre, Jacupiranga in relation to alkaline rocks of the Jacupiranga Alkaline Complex.

the silcrete zone (Fig. 6). Ce together with other REEs occur in concretions consisting of Mn oxides like todorokite, lithiophorite and romanechite together with goethite, clay minerals and silica. The high enrichment of Ce relative to the other REEs (Table 3) may be attributed to the immobilization of Ce after oxidation to Ce^{4+} and subsequent fixation in Mn oxides (Rankin and Childs, 1976; Glasby et al., 1987). The REEs most probably are derived from weathering products of nepheline-pegmatitic and syenitic veins, which form part of the semi-autochthonous laterite. Possibly under conditions of low pH and high CO_2 activity in the upper semi-autochthonous laterite, REEs become mobilized and transported in solution (Burkow and Podporina, 1967; Nesbitt, 1979; Plimer, 1989), perhaps bound to negatively charged Mn colloids. Rising pH and increasing concentration of the solution in oxidizing

environment above the less permeable silcrete zone favour the precipitation of Ce and other REES together with Mn. Microscopic observations revealed that REES are initially scavenged by freshly precipitated amorphous and non-stoichiometric Mn-Fe oxides, which have large surfaces and high adsorption capacities (Kühnel, 1989; Plimer, 1989). The low Ce content of the crystalline mineral phases indicates that during crystallisation, REES become released and partly removed. Normalization of the REE patterns of the Mn-Fe concretions to the REE patterns of the alkaline rocks which occur as nepheline-pegmatitic and syenitic veins in the dunite body shows distinct supergene enrichment of Ce and slight enrichment of the heavy REES Yb and Lu (Fig. 9).

The lower level of Ce enrichment at Jacupiranga (Fig. 6) coincides with the occurrence of *in-situ* weathering products of nepheline-pegmatitic veins, primarily rich in Ce and REES.

Drainage and geomorphology

The spatial distribution of Mn, Co and Ce in the laterites leads to the assumption that the behaviour of these elements is strongly controlled by local drainage conditions in the depressions of the peridotite karst. Probably due to relatively high mobility in colloidal solution, Mn, Co and Ce together with other REES migrate over some tens of meters towards the lowest portions of the depressions. This may result in concentration of these elements in the lower limonitic zone and further accumulation at the base of the depression where internal drainage temporarily is impeded and concentration of the solution is high. The highest Mn concentrations in Olympic (> 1.5 wt.% MnO) and the highest Ce concentrations in Jacupiranga (> 0.5 wt.%) occur in the lowest portion of the depression (Figs. 5 and 6).

SUMMARY AND CONCLUSIONS

Laterites overlying ultramafic complexes in Jacupiranga/Brazil and Las Buenas and Olympic/Philippines are products of a polygenetic evolution (Fig. 10).

During the first stages of weathering, Mn partly becomes mobilized from minerals such as olivine, pyroxene and serpentine in its bivalent oxidation state. Under positive Eh and alkaline conditions, silicate-bound Cr in contrast to Cr in resistant chrome-spinels is leached and depleted in the upper saprolite. Since it can account for more than 50% of the total Cr content of the ultramafics, this fact has to be taken into account when using total Cr as an internal standard for mass balances.

Semi-autochthonous laterites are only partly formed from the products of *in-situ* weathering of the ultramafic bedrock. High proportions of minerals

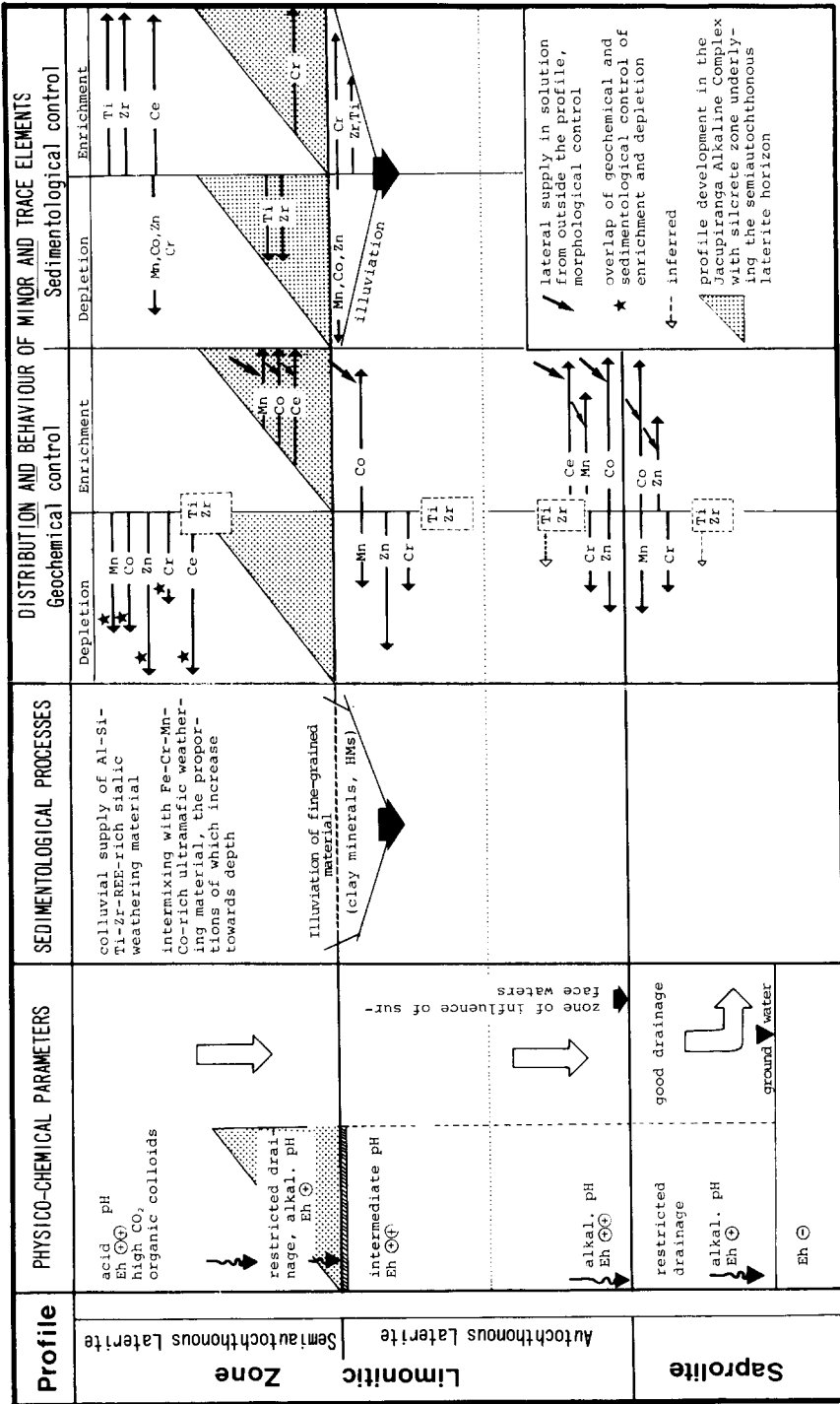


Fig. 10. Model of the behaviour of Mn, Co, Zn, Cr, Ti, Zr and Ce during the evolution of laterite profiles above ultramafic complexes, summarized from data of Las Buenas, Olympic and Jacupiranga; enrichment and depletion relative to the HIM content as internal standard.

like zircon, ilmenite, rutile, etc. indicate high proportions of weathering material derived from sialic rocks which intersect the ultramafics in form of dykes or occur in the vicinity of the ultramafic bodies. The abundance of this material in upper parts of weathering profiles produces unusually high concentrations and enrichment factors for Ti, Zr and REES.

One factor responsible for erosion and redeposition within ultramafic complexes is the high rate of solution which results in the formation of the peridotite karst. Karstification leads to the development of steep morphological gradients, thus enhancing the reworking of weathering profiles, short colluvial transport and final accumulation of kaolinite-rich sialic weathering material at the base of morphological depressions.

The close association of ultramafics with gabbros, troctolites, spilites and basalts in ophiolite sequences, the latter often occurring as dykes in ultramafic complexes, produces a considerable compositional inhomogeneity of the ultramafic body. This inhomogeneity and the proportions of sialic rocks relative to the ultramafics will to a certain degree be reflected in the composition of the semi-autochthonous laterites. In Las Buenas and Olympic, only a few individual gabbroic dykes cut the ultramafics. For this reason, the composition of the semi-autochthonous laterite is dominated by "ultramafic" Fe-Cr-rich weathering material (Table 4). In Jacupiranga, the serpentized dunite has undergone significant hypogene modification as a result of the intrusion of numerous nepheline-pegmatitic and syenitic dykes. The high abundance of these dykes is clearly reflected by high proportions of Ti-Zr-Al-Si-REE-rich material in the semi-autochthonous laterites (Table 4). Ti, Zr, Al and Si show highest concentrations at the base of the peridotite karst depressions, where semi-autochthonous laterites are usually well developed.

The gradual increase of sialic material towards the top of the semi-autoch-

TABLE 4

Calculation of the proportions of transported "sialic" weathering material per one part of residual "ultramafic" weathering material in semi-autochthonous laterites of Las Buenas, Olympic and Jacupiranga with HM contents as internal reference; modified after Schellmann (1987)

	Las Buenas, Profile 5-11	Olympic/TORO		Jacupiranga, Profile DUN 1
		Profile 15.0-10	Profile 15.5-10.75	
(A) Average HM content of the autochthonous laterite	3.36	3.4	3.2	4.5
(B) Average HM content of the semi-autochthonous laterite	2.18	3.1	2.1	1.0
Proportion of transported "sialic" weathering material per 1 part of residual "ultramafic" weathering material in semi-autochthonous laterite = $(A-B)/B$	0.54	0.1	0.52	3.5

thonous laterite is significant in all areas. The corresponding increase of Ti, Zr, Al and Si cannot be explained by mere depletion of Fe in this profile zone and downward dislocation. This process would have caused a dilution and decrease of the HM (chrome-spinel) contents in the Fe-rich ferruginous zone deeper in the profile, where Fe is likely to have precipitated. The correlation between the Fe content of the laterite matrix and the HM content (mainly chrome-spinel) of the laterites, however, is positive (Fig. 11). Mass balances indicate that no considerable absolute gain or loss of Fe has occurred (Friedrich et al., 1987b). The gradual increase of silic weathering material towards the profile top rather results from later erosion and redeposition of weathering material from silic rocks. Compared to ultramafics, silic and even alkaline rocks suffer less intensive weathering and disintegration. As a result, silic weathering material accumulates in the doline-like depressions of the peridotite karst and in the surface profile parts.

Leaching of the upper semi-autochthonous laterite in an oxidizing and moderately acid environment during later stages of the profile evolution mainly affects Mn, Co, Zn and REES. These elements migrate downward in the profile and also follow the hydrological gradient. They precipitate due to rising pH and increasing concentration of the solutions, leading to anomalously high concentrations of Ce and other REES, which are highly unusual for weathering products overlying ultramafics. The parameters which favour the enrichment of Ce and other REES in lateritic weathering profiles above ultramafics are:

- occurrence of ultramafic Mn-rich rocks and alkaline-peralkaline REE-rich rocks in close spatial association;
- formation of semi-autochthonous laterites;
- leaching of Ce and REES and their precipitation along geochemical barriers, i.e. silcrete zone; and
- existence of peridotite karst traps, which favour convergent groundwater

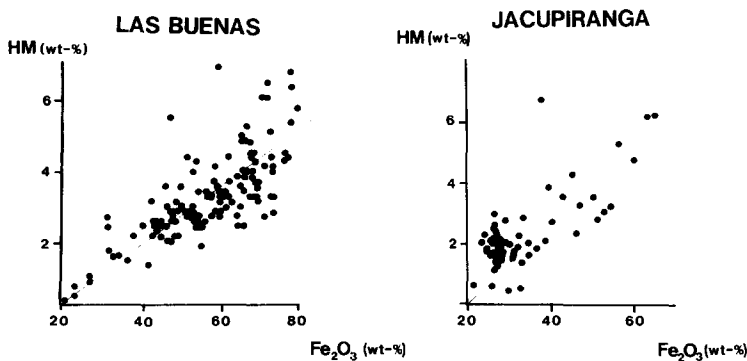


Fig. 11. Plot of the Fe₂O₃ contents of the lateritic fine fraction < 30 μm versus the HM contents of lateritic weathering products overlying ultramafic complexes of the Philippines and Brazil.

flow and accumulation of REE-enriched solutions in the base of small depressions.

Semi-autochthonous laterites are not restricted to the depressions of the peridotite karst, but may also occur as extensive weathering covers (Schellmann, 1989). Their camouflaging effect for the identification of ultramafic rocks and related mineralizations is common. Semi-autochthonous laterites are not restricted to ultramafic complexes, but are also reported to occur above other rock types (Kanig et al., 1989). Their existence must be taken into consideration for geological and geochemical surveys in tropical terrain.

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