SEÇÃO V - GÊNESE, MORFOLOGIA E CLASSIFICAÇÃO DO SOLO

IRON OXIDES IN PLINTHIC SOILS ON SEDIMENTARY DEPOSITS IN NORTHEASTERN BRAZIL(1)

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SUMMARY

This study was conducted to examine the distribution and nature of Fe oxides in plinthic soils on the sediments of Barreiras Group (in the state of Piauí) and Itapecuru Formation (in the state of Maranhão) in Northeastern Brazil. Four pedons were selected: a "plinthic, dystrophic, epieutrophic Gray Podzolic with low activity clay" and a "dystrophic Plinthosol with low activity clay" (both Plinthic Kandiustalfs) on the Barreiras sediments, as well as an "eutrophic Plinthosol with low activity clay" and an "allic Plinthosol with low activity clay" (both Plinthustalfs) on the Itapecuru sediments. Soil samples were fractionated into > 2 mm (pisoliths), water-stable aggregates (plinthite) and matrices; the aggregates and matrices were further fractionated into sand, silt and clay sizes. Dithionite extractable iron (Fe_d) and aluminum (Al_d), as well as oxalate extractable iron (Fe_o), were determined for all fractions, and X-ray diffraction analyses were performed on the pisoliths. It was observed that the Plinthustalfs contain more iron oxides, exhibit more extensive plinthite development and have a greater potential for further plinthite development than the Kandiustalfs. The distribution of values for the Fe_d indicates that plinthite formation and induration in all soils were accompanied by an enrichment of Fe oxides in all particle size fractions. This Fe segregation was accompanied by aggregation of particles leading to a greater degree of crystallinity, as indicated by analysis of the ratios of Al_d:Fe_d. Larger ratios of goethite to hematite, and relatively smaller amounts of silicates in the more mature pisoliths were revealed by X-ray diffraction analysis. Ratios of Al_d:Fe_d were larger in the Kandiustalfs than in the Plinthustalfs, and also larger than expected for Al-substituted Fe oxides. According to ratios of Al_d:Fe_d, Fe mobilization in all soils has likely occurred under reducing conditions, facilitated by organic matter on the soil surface.

Index Terms: plinthosol, Ustalf, Barreiras Group, Itapecuru Formation, citrate, dithionite, oxalate, X-ray diffraction, aluminum, goethite, hematite.

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RESUMO: *ÓXIDOS DE FERRO EM SOLOS PLÍNTICOS DE DEPÓSITOS SEDIMENTARES NO NORDESTE DO BRASIL*

O presente estudo foi conduzido com a finalidade de examinar a natureza e a distribuição de óxidos de ferro em solos plínticos desenvolvidos de sedimentos atribuídos ao Grupo Barreiras (no estado do Piauí) e à Formação Itapecuru (no estado do Maranhão), no nordeste do Brasil. Quatro perfis foram selecionados: um Podzólico Acinzentado argila de atividade baixa distrófico epieutrófico plíntico e um Plintossolo argila de atividade baixa distrófico (ambos "Plinthic Kandiustalfs"), desenvolvidos de sedimentos do Grupo Barreiras, e dois Plintossolos argila de atividade baixa álicos (ambos "Plinthustalfs"), desenvolvidos de sedimentos da Formação Itapecuru. As amostras de solos foram separadas em frações > 2 mm (pisolitos), agregados estáveis em água (plintita) e matriz; os agregados e a matriz foram posteriormente fracionados em areia, silte e argila. Foram efetuadas extrações de ferro (Fed) e alumínio (Ald), usando o extrator ditionito, e do ferro (Feo), usando oxalato, de todas as frações. Análise de difração de raios-X foi executada nos pisolitos. Observou-se que os plintossolos ("Plinthustalfs") da Formação Itapecuru contêm mais óxidos de ferro, exibem extensivo desenvolvimento de plintita e têm maior potencial para um grau ainda maior de desenvolvimento desta plintita, quando comparados ao Podzólico Acinzentado e ao Plintossolo do Grupo Barreiras ("Plinthic Kandiustalfs"). A distribuição dos valores de Fed indica que a formação de plintita e o endurecimento em todos os solos foram acompanhados por enriquecimento de ferro em todas as frações. A segregação de ferro foi acompanhada pela agregação de partículas, levando a um maior grau de cristalinidade, como indicado pela análise das razões Feo/Fed. Análise da difração de raios-X revelou maiores razões de goethita para hematita, bem como menores quantidades de silicatos nos pisolitos mais maturos. Razões Ald/Fed foram maiores no Podzólico que nos Plintossolos e, maiores que as esperadas para os óxidos de ferro com substituição por alumínio. De acordo com as razões Ald/Fed, é provável que a mobilização de ferro em todos os solos tenha ocorrido sob condições de redução, facilitada por matéria orgânica na superfície.

Termos de indexação: Plintossolo, Ustalf, Grupo Barreiras, Formação Itapecuru, citrato ditionito, oxalato, difração de raios-X, alumínio, goethita, hematita.

INTRODUCTION

The term plinthite was introduced into the vocabulary of pedology by the Soil Survey Staff (1975) to represent certain Fe-rich soil features. Eswaran et al. (1990) defined plinthite as: "... a discrete body of soil material with less than 25% by volume of rock structure which is the result of absolute accumulation of iron; is firm to very firm when moist and hard or very hard when dry; occurs as dark red mottles, which are usually in platy polygonal or reticulate patterns; the core of plinthic material may be hard and brittle but is crushed easily by the finger and in the process, smears the finger. On drying, plinthite hardens irreversibly to petroplinthite."

According to Sanchez & Buol (1975), approximately five percent of the soils in Central Brazil contain plinthite at or near the surface. The third approximation of the Brazilian System of Soil Classification (EMBRAPA, 1988) has defined a plinthic horizon (designated by 'f', corresponding to 'v' in Soil Taxonomy) as a B or C horizon containing at least 15% plinthite and having a thickness greater than 15 cm. This horizon is diagnostic for the class of soils called Plintossolo, a concept maintained in the recently published fourth approximation of the system (EMBRAPA, 1997).

In general, plinthite formation first requires the accumulation of Fe oxides, usually into mottles, which occurs mainly through reductive dissolution, translocation, followed by oxidative reprecipitation (van Schuylenborgh, 1971; van Breemen, 1988). Eventually, adjacent soil particles become sufficiently cemented by Fe oxides to form a stable aggregate called plinthite. This enrichment stage may take from decades to millions of years, depending on the mineralogical source of Fe and whether it must be transported from other parts of the soil profile or landscape (van Breemen, 1988). Once formed, plinthite can harden into petroplinthite in as little as one year (Ahmed & Jones, 1969). The change in consistency results from large concentrations of Fe oxides, a high degree of crystallinity and large crystal size (McFarlane, 1976; Comerma et al., 1977; Eswaran et al., 1980).

Research has shown that plinthite induration influences root development and soil solution movement as well as many physical-chemical properties, such as ion exchange and fixation (Carlan et al., 1985; Blume et al., 1987; Eswaran et al., 1990). However, due to the vague definitions and complexity of its formation, the behavior and influence of plinthite remains poorly understood (Krishnaswamy, 1981; Melfi & Carvalho, 1983; McFarlane, 1987; Ogura, 1987). A recent study of a toposequence of soils containing plinthite further illustrated the influence of landscape evolution on the development of such soils (dos Anjos et al., 1995). This research examines, from a genetic standpoint, the Fe and Al oxides present in different consistency and particle size fractions of plinthic soils developed from Barreiras Group and Itapecuru Formation sediments in Northeastern Brazil.

MATERIAL AND METHODS

The pedons examined in this study are representative of two groups of plinthic soils in Northeastern Brazil (Table 1). According to the Köppen system, the climate is classified as Aw and the rainy season from February to April is preceded by distinct dry season (Jacomine, 1986a,b). Two other pedons (B1 and B2), developed from the kaolinitic sandstones of the Tertiary Barreiras Group, were selected from the state of Piauí, where the annual rainfall is between 1.200 and 1.600 mm (Jacomine, 1986a). Two other pedons (I1 and I2), developed from the finely-granulated, clayey sandstones of the Inferior Cretaceous Itapecuru Formation, were obtained from the state of Maranhão, with an annual rainfall of 1.600 and 1.800 mm (Jacomine, 1986b).

Pedon B1 is classified as "Podzólico Acinzentado argila de atividade baixa distrófico epieutrófico plíntico abrupto A moderado textura arenosa/média fase floresta/caatinga relevo plano" and pedon B2 is a "Plintossolo argila de atividade baixa distrófico A moderado textura arenosa/média fase floresta/caatinga relevo plano" (Jacomine, 1986a). Pedon I1

Table 1. Organic carbon content, bulk density as well as distribution of soil material among each consistency and particle size fraction

Horizon	Depth	O.C.	Bulk density	Matrix	Soil aggregate	> 2 mm(1)	Matrices			Aggregates		
							Sand	Silt	Clay	Sand	Silt	Clay
	cm	$g\ kg^{-1}$	$Mg\ m^{-3}$	%								
Pedon B1	Plinthic Kandiustalf			(3°3'S 41°45'W)(2)		(EMBRAPA ref. # pl-02-PI)						
A	0-10	7.4	1.46	88	10	2 (0)	94	5	1	92	6	2
E	10-25	3.0	1.55	85	13	2 (0)	90	6	4	96	3	1
Bt1	25-65	2.4	1.59	90	8	2 (0)	82	11	7	82	13	5
Bt2	65-110	2.1	1.63	80	19	1 (0)	82	12	6	83	12	5
Btf	110-155	2.1	1.66	46	36	18 (84)	65	22	13	73	20	7
BCx	155-200	1.0	1.61	89	9	2 (0)	72	20	8	82	16	2
Pedon B2	Plinthic Kandiustalf			(3°5'S 41°45'W)(2)		(EMBRAPA ref. # pl-04-PI)						
A	0-8	5.1	1.47	99	no	1 (0)	93	5	2	no	no	no
E1	8-60	1.8	1.57	99	no	1 (0)	93	4	3	no	no	no
E2	60-115	1.6	1.60	90	9	1 (3)	89	7	4	88	9	3
Btf	115-170	1.5	1.79	78	21	1 (22)	61	17	22	64	17	19
BCf	170-220	0.8	1.75	78	20	2 (0)	70	22	8	69	17	14
Pedon I1	Plinthustalf			(3°18'S 44°26'W)(2)		(EMBRAPA ref. # pl-05-MA)						
A	0-12	14.0	1.41	37	62	1 (24)	78	19	3	74	18	8
E	12-25	6.6	1.52	70	25	5 (98)	68	21	11	73	24	3
Ec	25-52	6.0	1.97	18	3	79 (100)	59	17	24	23	9	68
Btf1	52-80	4.6	1.60	90	3	7 (100)	34	34	32	35	36	29
Btf2	80-135	2.5	1.67	90	6	4 (100)	46	45	9	50	29	21
BCf	135-200	1.9	1.56	76	24	tr. (100)	50	27	23	80	16	4
Pedon I2	Plinthustalf			(3°22'S 44°24'W)(2)		(EMBRAPA ref. # pl-07-MA)						
Ac1	0-10	13.2	1.93	39	3	58 (100)	64	24	12	78	16	6
Ac2	10-42	6.8	2.38	24	3	73 (100)	50	34	16	50	25	25
Bt	42-60	4.4	1.53	87	4	9 (100)	34	31	35	50	19	31
Btf1	60-80	2.9	1.50	81	10	9 (100)	25	32	43	37	35	28
Btf2	80-110	2.1	1.58	83	10	7 (100)	23	41	36	51	34	15
Btf3	110-160	1.7	1.62	82	15	3 (100)	21	44	35	42	53	5
BCf	160-200	1.2	1.65	87	11	2 (100)	25	46	29	43	38	19

(1) Values in parentheses indicate percentage of > 2 mm fraction that is pisoliths. (2) Approximate latitude and longitude of profile sites. no: no fraction; tr: trace; O.C.: organic carbon.

is a “Plintossolo argila de atividade baixa/argila de atividade alta eutrófico A moderado textura média/ argilosa fase floresta tropical subperenifólia dicótolo-palmánea relevo plano” and pedon I2, a “Plintossolo argila de atividade baixa álico A moderado textura média muito cascalhenta/argilosa fase pedregosa II (concrecionária) floresta tropical subperenifólia dicótolo-palmánea relevo suave ondulado” (Jacomine, 1986b). According to Soil Taxonomy (Soil Survey Staff, 1994), the Barreiras pedons are Plinthic Kandiustalfs and the Itapecuru pedons are Plinthustalfs, with greater than 50 percent plinthite by volume.

Soil bulk density was determined by a paraffin-coated clod method (EMBRAPA, 1979). Organic carbon (OC) was determined by the National Soil Mapping and Conservation Service (SNLCS), using a modification of the Walkley-Black method (EMBRAPA, 1979). Other physical and chemical poperties of these soils can be obtained in Heck (1994).

A modification of the technique described by Daniels et al. (1978) was selected for the initial separation of soil horizon samples into consistency fractions (Table 1). Approximately 250 g of air-dry soil was placed on a 12 cm diameter, 2 mm sieve, and submerged in deionized water. After 2 h, the sample was agitated vertically at a rate of 35 cycles per min for 1 h, through a stroke length of 3.7 cm. A two-hour rest period followed by 1 h of agitation was performed two more times (continuous submersion). Material which passed through the sieve during these 9 h was considered to be matrix material. The material remaining on the sieve (composed of water-stable aggregates and > 2 mm fraction) was air-dried and then resubmerged for 2 h. Finally, the water-stable aggregates were separated from the > 2 mm fraction by crushing them between fingers and passed through the sieve; this consistency fraction included material considered to be plinthite. The > 2 mm fraction was composed of both primary mineral grains as well as Fe oxide pisoliths.

Both the matrix and water-stable aggregates of each horizon were subsequently separated into size fractions (Table 1). The material was dispersed by ultrasonification (Jackson, 1979) and the sand fraction removed by sieving (0.05 to 2 mm fraction). Separation of the silt (2 to 50 µm) and clay (< 2 µm) fractions was achieved by centrifugation (Jackson, 1979). All fractions were freeze-dried after fractionation.

Extractions of Fe and Al by sodium dithionite citrate (Fe_d and Al_d) and Fe by acid-(pH 3) ammonium oxalate (Fe_o) were performed according to the techniques of Sheldrick (1984). The clay and silt fractions were utilized directly, but the sand fraction and pisoliths were first crushed with an agate mortar and pestle to pass a 0.5 mm sieve. Analysis of the extracts was performed on a Perkin Elmer 3100 atomic absorption spectrophotometer. Values of Fe_d, Al_d and Fe_o for the matrices and water-stable aggregates were calculated from size separates. The mineralogy of the pisoliths was determined on material crushed to pass a 0.5 mm sieve, using a Philips PW 1301 X-ray diffractometer (Mn-filtered, Fe-Ka radiation) equipped with a spinning powder holder.

RESULTS AND DISCUSSION

Concentration of Fe in citrate-dithionite extracts

The extraction of Fe_d (Table 2), revealed much greater concentrations of Fe oxides in the pedons developed from the Itapecuru sediments (I1 and I2) than in those from the Barreiras sediments (B1 and B2). This difference was observed in all particle size and consistency fractions. Generally, the Fe_d increased from the matrix to water-stable aggregates to pisoliths in both pedon groups, a trend evident in all size fractions. In the Barreiras pedons, the concentration of Fe_d was also greater in the finer size fractions. Such behavior was observed only in certain horizons of the Itapecuru pedons; in others, the coarser fractions usually contained more Fe_d.

The concentration of Fe_d in each fraction (Table 2) combined with the relative distribution of material among the consistency and size fractions (Table 1), yields the distribution of Fe_d within each horizon (Figure 1). With the exception of the Btf horizon of B1 and the BCf of B2, more than half of the Fe_d in the Barreiras pedons is still located in the matrices. In the Itapecuru pedons, however, most Fe_d is already segregated into water-stable aggregates and pisoliths, especially in the concretionary horizons, where almost all Fe_d is in pisoliths. In both groups of pedons, the proportion of Fe_d associated with the sand fraction was generally greater for the water-stable aggregates than for the surrounding matrix; this was usually balanced by a smaller proportion of Fe_d in the clay fraction.

To compensate for differences in the bulk density of each horizon (Table 1), the concentration of Fe_d in equivalent depth segments was calculated for each pedon (Table 3). The values obtained for the 0-200 cm segment show that the Itapecuru pedons contain greater than one order of magnitude more Fe oxides than the Barreiras pedons. Furthermore, whereas in the Barreiras pedons most Fe_d is located in the lower portion of the profile, most is located near the surface in the Itapecuru pedons. Although the two Itapecuru pedons contain very similar amounts (except in the 0-25 cm layer) and vertical distribution of Fe oxides, this is not the case in the two Barreiras pedons studied.

Ratio of Fe in oxalate and dithionite-citrate extracts

As illustrated in figure 2, the ratio of Fe_o:Fe_d is generally higher in the matrices than in the water-

Table 2. Concentration of Fe_d in the three consistency fractions, in the particle size fractions of the matrices and water-stable aggregates, as well as in the water-stable aggregates after potential isovolumetrical enrichment with Fe available in associated matrix(1)

Horizon	Matrix	Soil		Matrices			Aggregates			Enriched(1)
		Aggregate	> 2 mm(1)	S	Si	C	S	Si	C	aggregates
	g kg^{-1}									
					Pedon B1					
A	0.4	0.5	no	0.2	2.0	4.4	0.3	1.3	8.2	4
E	0.5	0.4	no	0.1	1.7	6.3	0.3	2.5	9.3	4
Bt1	0.9	0.9	no	0.2	2.3	6.3	0.2	2.6	8.2	11
Bt2	0.8	1.2	no	0.2	2.6	7.3	0.5	2.9	8.2	4
Btf	3.2	16.1	107	0.5	7.0	10.4	13.8	19.8	28.2	20
BCx	0.7	0.9	no	0.1	1.7	3.8	0.4	2.3	6.3	8
					Pedon B2					
A	0.2	no	no	0.1	1.1	4.3	no	no	no	no
E1	0.3	no	no	0.2	1.2	4.4	no	no	no	no
E2	0.4	0.6	no	0.1	2	4.9	0.1	3.1	5.9	5
Btf	3.1	6.1	no	0.2	7.5	7.9	1.4	14.5	13.8	17
BCf	1.1	2.3	154	0.2	2.9	4.4	0.8	6.1	5.5	6
					Pedon I1					
A	4.9	4.7	280	3.4	8.6	20.2	2.3	8.2	18.2	8
E	8.9	7.5	407	5.6	10.8	25.2	5.8	9.4	35.1	31
Ec	39.7	49.6	340	46.3	25.8	33.6	139.2	28.0	21.4	212
Btf1	24.6	91.6	300	26.8	27.4	19.0	127.8	87.8	52.9	486
Btf2	14.6	61.3	287	15.4	13.3	12.5	78.6	48.9	36.4	231
BCf	7.4	79.9	188	6.1	8.0	9.7	88.5	40.1	61.7	101
					Pedon I2					
Ac1	43.8	78.5	341	51.5	11.5	68.7	91.5	17.6	71.9	437
Ac2	29.2	44.0	426	42.0	4.7	40.7	53.8	13.2	55.4	235
Bt	35.9	47.7	433	21.7	21.6	62.7	39.7	30.2	72	497
Btf1	31.0	80.7	346	25.6	21.5	41.1	103.6	71.4	62.1	273
Btf2	16.4	55.6	256	18.4	13.2	19.0	71.8	34.3	48.7	172
Btf3	9.8	73.2	316	4.3	6.6	17.3	91.4	60.4	56.6	119
BCf	13.2	40.4	250	31.2	6.3	8.6	55.2	27.4	32.4	132

(1) assumes complete transfer of Fe from the matrix to existing aggregates; calculated according to Equation 1 in the text.
no: no fraction.

stable aggregates and pisoliths for both groups of pedons. Moreover, ratios for the finer size fractions tend to be smaller at depth; this is especially evident in the silt and clay fractions of the Itapecuru pedons. Although similar ratios were observed in the silt and clay fractions in both groups of pedons, the Barreiras pedons had larger ratios for the sand fraction. In the Itapecuru pedons, the Fe_o:Fe_d ratios for the sand fraction were much smaller than those for the silt and clay fractions; the silt fraction also exhibited smaller ratios than the clay at depth, but the trend was reversed near the surface. No consistent trends were observed among the particle size fractions in the Barreiras pedons, but the silt frequently had larger ratios than the clay.

X-ray diffraction analysis of pisoliths

X-ray diffraction (XRD) analysis revealed that the pisoliths isolated from these pedons were generally composed of Fe oxides (dominantly hematite and goethite), quartz and smaller amounts of kaolinite. Microcline was evident only in pisoliths from the deeper horizons of the Itapecuru pedons (Figure 3). Comparison of the quartz (100), goethite (110) and hematite (110) reflections revealed a decrease in the relative concentration of quartz near the soil surface of pedons I1 and I2. Furthermore, according to the relative intensities of the 110 reflections for goethite and hematite, the pisoliths near the surface of the Itapecuru pedons contain a greater proportion of goethite than those at depth.

Al:Fe Ratio in citrate-dithionite extracts

The Al_d:Fe_d ratios in matrices, water-stable aggregates, and all particle size fractions of the Barreiras pedons are generally much larger than those of the Itapecuru pedons (Figure 4). In fact, the Al_d:Fe_d ratios for the matrices and water-stable

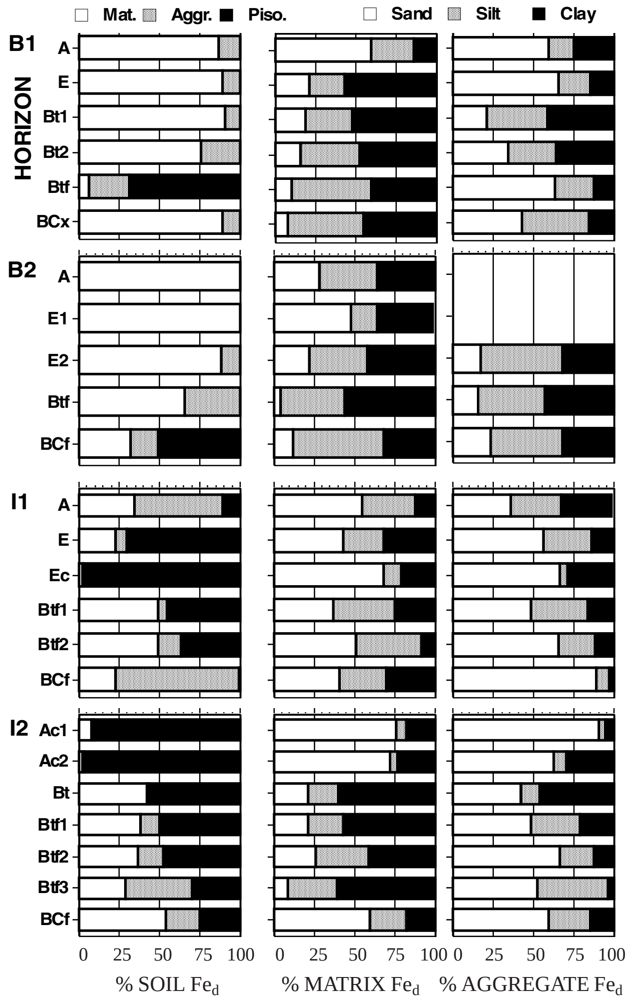

Figure 1. Distribution of Fe_d among the three consistency fractions and among the particle size fractions of the matrices and water-stable aggregates. Note that the horizontal scale is identical for all graphs and the legend for consistency fractions applies only to graphs in the first column.

aggregates of the Barreiras pedons normally exceed 0.5. In most horizons of the Itapecuru pedons, the ratio Al_d:Fe_d decreased from the matrices to water-stable aggregates (a tendency also observed in the various particle size fractions, especially at depth) and then to the pisoliths. Furthermore, the sand fraction exhibits smaller Al_d:Fe_d ratios than the other size fractions, with clay often exhibiting the largest ratios. In the Barreiras pedons, the pisoliths also exhibit the smallest Al_d:Fe_d ratios; however, though the water-stable aggregates have smaller ratios than the matrices in pedon B2, the opposite trend is observed in pedon B1. The Al_d:Fe_d ratios generally decreased with decreasing particle size in the Barreiras pedons. Within the Itapecuru pedons, the pisoliths exhibit lower Al_d:Fe_d ratios at greater depths.

Table 3. Concentration of Fe_d calculated for selected layers of the pedons studied$^{(1)}$

Layer	Pedon			
	B1	B2	I1	I2
cm	g kg^{-1}			
0-25	0.2	0.1	6.2	156.0
25-50	0.4	0.1	137.0	139.0
50-100	0.7	0.3	40.3	42.6
100-150	15.4	2.4	21.6	23.8
150-200	2.4	2.8	19.3	18.6
0-200	19.1	5.7	224.4	380.0

$^{(1)}$ based on bulk densities in Table 1 and Fe_d concentrations in Table 2.

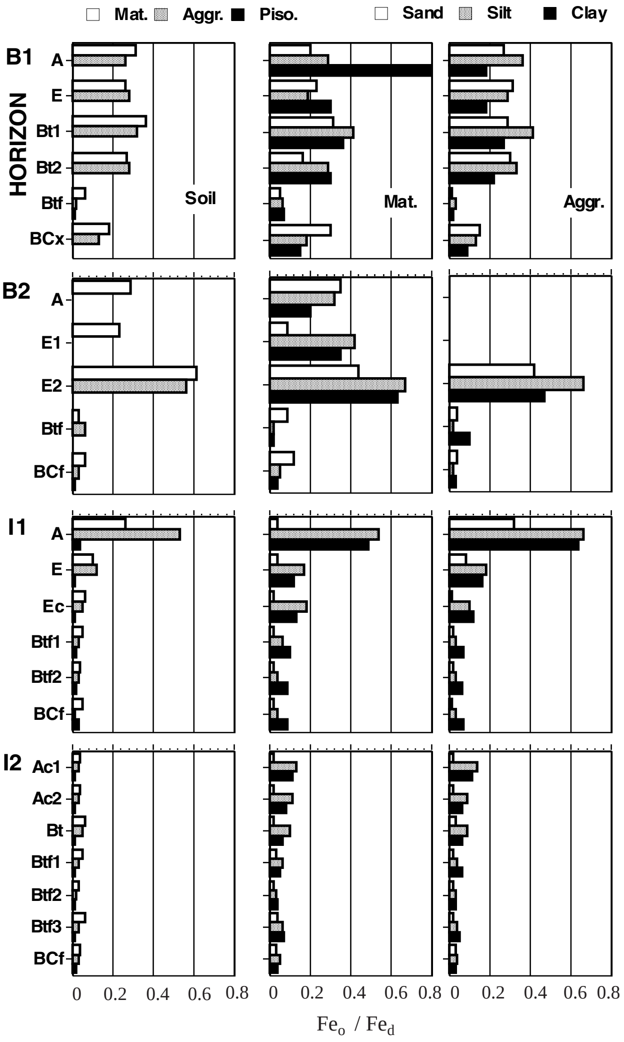

Figure 2. Ratio of Fe_o to Fe_d in each consistency fraction and in the particle size fractions of the matrices and water-stable aggregates. Note that the horizontal scale is identical for all graphs and the legend for consistency fractions applies only to graphs in the first column.

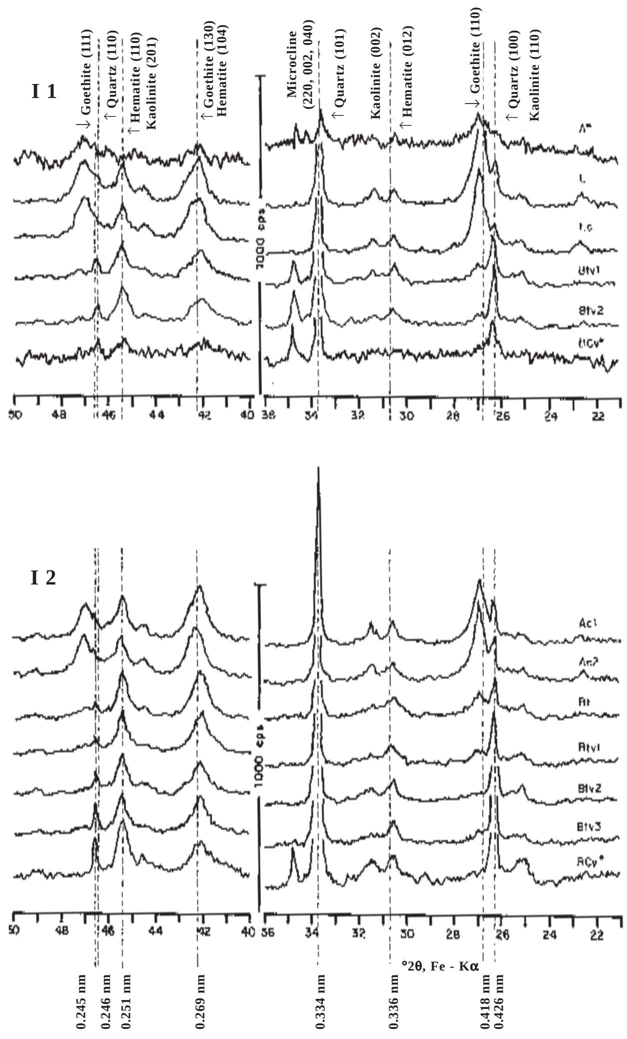

Figure 3. Partial powder X-ray diffractograms of the pisoliths in the > 2 mm phase. Patterns of horizons marked with '*' have cps scale expanded 2x.

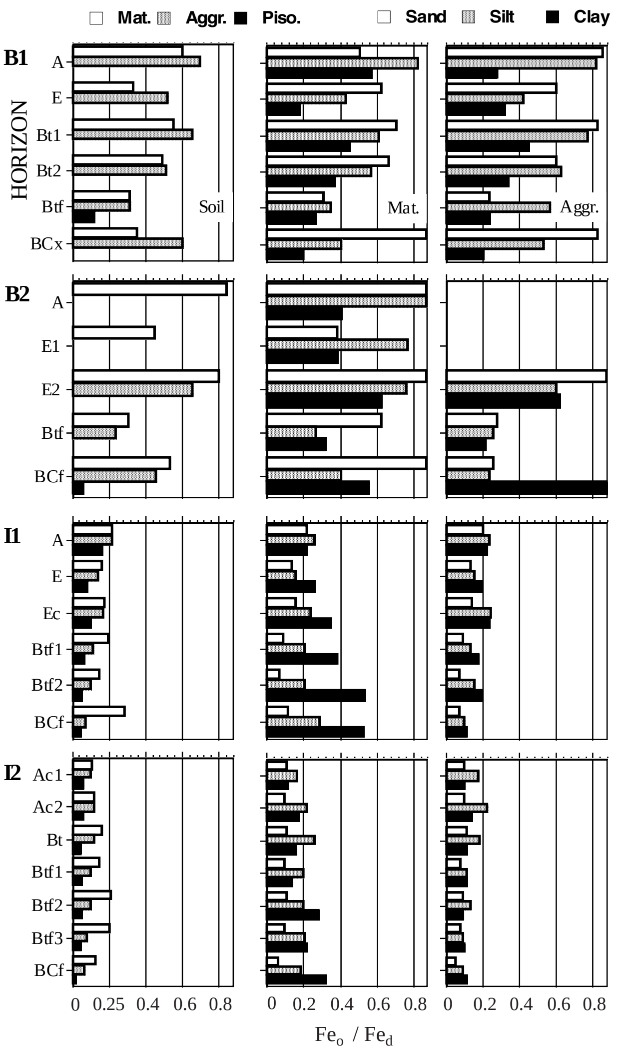

Figure 4. Molar ratio of Al_d to Fe_d in the three consistency fractions and the particle size fractions of the matrices and water-stable aggregates. Note that the horizontal scale is identical for all graphs and the legend for consistency fractions applies only to graphs in the first column.

Pedogenic redistribution of Fe oxides

Although both groups of pedons were reported to have imperfect internal drainage (Jacomine, 1986a,b), and, despite greater rainfall in the Itapecuru pedons, the smaller quantity of Fe oxides in the Barreiras pedons suggest that they have experienced more extensive leaching. This is further supported by the absence of easily weathered minerals in these pedons, according to petrographic and XRD analyses (Heck, 1994); Bossi et al. (1982) reported Fe-bearing minerals in sediments of the Barreiras Group. In contrast, biotite was observed in the sand fractions of the Itapecuru pedons (Heck, 1994) and other soils developed from these sediments (dos Anjos et al., 1995). The accumulation of Fe in the Btv horizon of B1 can be attributed to the low permeability of the underlying fragipan (BCx).

The distribution and concentration of Fe_d in the Itapecuru pedons (Tables 2 and 3, Figure 1), appear to be truncated versions of what McFarlane (1976) calls "Immature (Spaced Pisolithic) Groundwater Laterite". Pedon I1 is currently located on a level of the landscape, whereas I2 occurs in a summit position. Ultisol profiles with similar morphology, but slightly smaller concentrations of Fe, were described by dos Anjos et al. (1995): one similar to I1 occurred in a footslope position and another similar to I2 in a shoulder position. As such, the relatively Fe_d-poor A and E horizons underlain by an Ec horizon in I1 (Table 2), absent in I2, probably reflect a colluvial deposition after truncation. Similarities in the OC contents suggest, however, that neither pedon has experienced extensive erosion or deposition recently (Table 1).

Given the proximity (approximately 11 km) and the similarity in elevations (about 40 m above sea) of these two pedons, it is conceivable that they were once influenced by a common regional groundwater table. The smaller proportion of Fe_d in the form of pisoliths in the BCv horizon of I1, could also reflect less pronounced wetting and drying cycles than in I2, due to current differences in their landscape positions. Schwertmann & Fanning (1976) also explained a zone of maximum mottling below a zone of maximum pisolith formation by more prolonged wetness.

Plinthite formation and induration

The relative concentrations of Fe_d in the three consistency fractions of most horizons, i.e., pisoliths > water-stable aggregates > matrix (Table 2), reflect the importance of Fe oxides as cementing agents in the plinthite and petroplinthite. In horizons where the matrix was found to contain more Fe_d than the water-stable aggregates (certain A and E horizons), there is probably greater influence of organic matter on aggregate stability (Table 1). This is supported by the larger ratios of Fe_o:Fe_d near the soil surface of these pedons, resulting from the perturbation of crystal growth by organic compounds (Schwertmann, 1966).

The larger proportion of Fe_d in the water-stable aggregates that is associated with the sand fraction (and smaller proportion associated with the clay fraction), compared with that in the matrices (Figure 1), indicates a tendency for the Fe oxides to aggregate with other particles during enrichment. This is anticipated since the precipitation of Fe on an existing surface is thermodynamically favored over the creation of a new precipitation nucleus (Stumm & Morgan, 1981). The process is not exclusive, however, because the concentrations of Fe oxides in all size fractions of the water-stable aggregate are greater than those in the associated matrix (Table 2).

Assuming that Fe_d reflects pedogenic Fe oxides, and Fe_o reflects the reactive surface area of Fe oxides (Boaggard, 1990), smaller ratios of Fe_o:Fe_d should indicate a greater degree of aggregation or longer range crystallinity. Accordingly, the degree of aggregation of Fe oxides in these soils generally increases from the matrix to water-stable aggregates and then to pisoliths (Figure 2). Similar behavior was observed in the Ultisols developed from the Itapecuru sediments (dos Anjos et al., 1995). The Fe_o:Fe_d ratios observed for the size fractions in the Itapecuru pedons also suggest an increasing degree of aggregation of Fe oxides with increasing particle size (extending into the > 2 mm fraction which contains the pisoliths).

Although hematite and goethite tend to aggregate with themselves (Schwertmann & Kämpf, 1985), the larger specific surface area of Fe oxides with short range crystallinity (such as ferrihydrite) makes them more effective at binding clay particles into microaggregates (Arduino et al., 1989; Barberis et al., 1991). This mechanism can explain the larger Fe_o:Fe_d ratios frequently encountered in the clay and especially in silt fractions (Figure 2). Furthermore, in comparison with the Itapecuru pedons, a larger proportion of the Fe oxides associated with the sand of the Barreiras pedons is likely to be ferrihydrite precipitated on the surface of other grains.

Al Substitution and mechanism of Fe mobilization

As with the total Fe content of these soils, the higher Al_d:Fe_d ratios observed in the various fractions of the Barreiras pedons, compared with the Itapecuru pedons (Figure 4), could be due to parent material or preferential leaching of Fe in the Barreiras pedons. According to Schwertmann & Taylor (1989), a molar ratio of 0.5 (possible in goethite) represents the maximum Al for Fe substitution in Fe oxides; therefore, higher values could indicate the presence of poor crystalline Al oxides or aluminosilicates. Although it is not possible to reject the possibility of Al oxides in the Itapecuru pedons, their Al_d:Fe_d ratios can be explained by Al-substituted Fe oxides. Indeed, most of the ratios for the I1 and I2 are below 0.2, which corresponds to the maximum substitution of Al in hematite (Schwertmann & Taylor, 1989). The Ultisols examined by dos Anjos et al. (1995), with similar (to I2) or slightly smaller (than I1) Al_d:Fe_d ratios, did not contain detectable amounts of gibbsite, either.

The decrease in Al_d:Fe_d observed with the increase in particle size as well as from matrix to water-stable aggregate pisolith, suggests that the development of the plinthite and petroplinthite has occurred during periodic anaerobic conditions. Reducing conditions favor the mobilization and segregation of Fe over Al (Fitzpatrick & Schwertmann, 1982); the bauxitization of laterites has been attributed to such processes (Jeanroy et al., 1991). This mechanism can also explain the lower Al_d:Fe_d ratios found in pisoliths at depth in the Itapecuru pedons.. The lower Al_d:Fe_d ratios observed in some clay (compared with silt) fractions could have also resulted from reductive solubilization of Fe from water-stable aggregates or pisoliths, followed by precipitation in the matrices of the same horizon, as can occur under pseudogleization. Both energy and electrons for chemical reduction are currently abundant in the organic matter present in the surface horizons (Table 1). However, since pedon I2, classified as ‘allic’ (> 50% exchangeable Al), generally exhibited lower Al_d:Fe_d ratios than pedon I1, the present suite of Al and Fe oxides does not reflect current conditions.

Whereas the conversion of ferrihydrite to hematite can occur by dehydration, the formation of goethite occurs by precipitation from the solution phase (Schwertmann & Taylor, 1989). Preferential reductive dissolution of hematite (Torrent et al., 1987), followed by precipitation of goethite and/or translocation of Fe could also explain the lower hematite/goethite ratios observed near the surface. The reduction and oxidation of Fe oxides create very intense weathering conditions (alkaline and acid, respectively) which accelerate the dissolution of silicate minerals. Such a process is also likely responsible for smaller quantities of quartz and microcline in the older pisoliths (Brinkman, 1970; Ambrosi et al., 1986; Amouric et al., 1986; van Breemen, 1988). Batista & Santos, (1995) have also shown micromorphological evidence of ferrolysis (acidification due to oxidation of Fe) in these soils.

Potential for further development

Considering the fractionation method used, the smaller Fe_d concentrations in the water-stable aggregates of pedon B1 and B2, compared with I1 and I2 (Figure 1), suggest that plinthite formation on the coarser-textured Barreiras sediments requires less Fe oxide than on the Itapecuru sediments (Table 1). However, based on Fe_d of the matrix fraction, only certain horizons in pedons I1 and I2 contain sufficient Fe oxides to enrich existing plinthite to concentrations similar to that observed in associated pisoliths (Table 2). These Fe_d concentrations were calculated assuming that Fe oxides in the matrix of a horizon could be translocated into the associated water-stable aggregates without causing a change in aggregate volume, according to the equation:

$$\text{Fe}_\text{d} \text{ in Enriched Aggregates} = \frac{\text{Mass Fe}_\text{d} \text{ in Aggregates} + \text{Mass Fe}_\text{d} \text{ in Matrix}}{\text{Mass of Aggregates} + \text{Mass Fe}_\text{d} \text{ in Matrix}} \quad (1)$$

Due to the paucity of easily weatherable minerals in the Barreiras pedons and some horizons in the Itapecuru pedons, isovolumetric enrichment of plinthite would require the translocation of Fe from other parts of the soil profile and/or landscape. In these cases, however, the transformation of plinthite to petroplinthite could still occur by either the inward migration of Fe (decreasing aggregate volume) or by the formation of a Fe oxide-rich crust (Eswaran et al., 1980). Energy dispersive X-ray analysis of selected pisoliths from these pedons showed crusts with higher Fe concentrations (Heck, 1994).

CONCLUSIONS

1. The Itapecuru pedons exhibit a much greater degree of plinthite and petroplinthite formation as well as a potential for further development than the Barreiras pedons.

2. The development of plinthite and petroplinthite in these profiles was apparently influenced by the following processes: mobilization of Fe under predominantly reducing conditions, a segregation of Fe oxides and a concurrent increase in their degree of aggregation to form plinthite and, eventually, petroplinthite, in which a transformation of hematite into goethite and dissolution of silicates, occur.

3. Although the finer-textured Itapecuru soils are more conducive to retention of Fe oxides, they apparently require greater concentrations for the formation of plinthite than do the Barreiras soils.

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