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Formation of soils with plinthite on a toposequence in Maranhão State, Brazil

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Abstract

Soils with plinthite and ironstone concretions are extensive in Maranhão State, northeastern Brazil. They formed from the Fe-rich Itapecurú sandstone in a tropical subhumid climate with distinct wet and dry seasons. Most plinthic soils in Brazil have properties associated with low-activity clays, but these soils were reported to have properties associated with high-activity clays.

The main objectives of this study were to characterize the chemical and mineralogical properties of the soils and to deduce the processes of their formation in relation to hillslope position. Six soils were sampled, two each on summit, shoulder, and footslope positions. They were analyzed by standard characterization methods and by X-ray diffraction and infrared spectroscopy. The parent sandstone bedrock contained mainly quartz, feldspars, muscovite, biotite, and resistant minerals in the sand fraction, and smectite, mica and kaolinite in the clay fraction. The main Fe-oxide mineral was hematite. Most soil horizons had lower Fe concentrations than the sandstone parent material. Kaolinite, mica and quartz occurred in the coarse clay fraction of all pedons.

Soils on the summit positions (Ustic Dystropept and Typic Ustorthent) lacked redoximorphic features, lacked plinthite, had the highest cation exchange capacity, and showed the weakest development. They were rich in smectite, probably inherited from the parent material, and goethite. Soils on shoulder positions (Inceptic Plinthustult and Plinthic Dystropept) had the largest concentration of total Fe, mostly as goethite. Those on footslopes (Typic Plinthaquult and Plinthic Paleaquult) exhibited the most redoximorphic features and had horizons in which the Fe was strongly concentrated in ironstone and plinthite, mostly as lepidocrocite and goethite. The crystallinity of these minerals increased from non-plinthic material to plinthite to ironstone concretions. They formed as the hematite in the sandstone weathered. These soils are less weathered than most plinthic soils of Brazil.

Diagnostic criteria for some subgroups of the Plinthustult and Dystropept great groups of Soil Taxonomy and some new classes for the Brazilian Soil Classification system were proposed.

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1. Introduction

According to Keys to Soil Taxonomy (Soil Survey Staff, 1992), "Plinthite (Gr. *plinthos*, brick) is an iron-rich, humus-poor mixture of clay with quartz and other dilutents. It commonly occurs as dark red redox concentrations which usually form platy, polygonal, or reticulate patterns. Plinthite changes irreversibly to an ironstone hardpan or to irregular aggregates on exposure to wetting and drying. In a moist soil, plinthite is soft enough to cut with a spade. After irreversible hardening, it is no longer considered plinthite but is called ironstone." This definition outlines the *maximum* hardness of plinthite. Apparently it must also have a *minimum* hardness or degree of cementation in the profile because it does not slake in water (Wood and Perkins, 1976a,b). Daniels et al. (1978) proposed a modification of this slaking test to identify material that has already hardened irreversibly. Plinthite has a high content of iron and/or aluminum relative to other components; Fe may be in the form of goethite, hematite, or poorly crystallized oxide compounds (Alexander and Cady, 1962).

Soils with plinthite and/or ironstone (petroplinthite) are common in northeastern Brazil. A reconnaissance soil survey of the State of Maranhão (EMBRAPA, 1986) showed that associations of soils in which Plinthosols are the main component constitute approximately 44,000 km^2 (13.5%) of the whole state. The class Plinthosols, recently introduced in the Brazilian Soil Classification System (EMBRAPA, 1980), includes soils with plinthic horizons which must be at least 15 cm thick and contain at least 15% plinthite by volume at specific depths (Camargo et al., 1986). In Keys to Soil Taxonomy (Soil Survey Staff, 1992) these soils are included in the Alfisol, Inceptisol, Oxisol, and Ultisol orders. In that classification system the occurrence of plinthite is considered to be an additional differentiating characteristic, not a diagnostic horizon, and the definition of plinthic subgroups is not complete.

Wood and Perkins (1976a) found that Fe was present mainly as hematite and goethite in the plinthite of some soils of the Southern Coastal Plain in the United States. In some soils of Venezuela, Daugherty and Arnold (1982) reported that SiO_2/Al_2O_3 molar ratios of plinthite ranged from <2 to >4, suggesting a wide range in mineral composition, while the cation exchange capacity ranged from 15 to 66 cmol$_c$ kg^{-1} of clay, indicating that these mottled zones are not always associated with low-activity clays. A scanning electron microscope study of the micro structure of concretionary lateritic soils from Northeast Brazil revealed structures ranging from a highly-cemented type without apparent voids to a structure with voids and a low degree of cementation (Carvalho, 1983). The material surrounding the voids contained fine particles of kaolinite, goethite, and hematite. Overall, however, little is known about other Plinthosols and plinthic Podzolic soils of northeastern Brazil.

The objectives of this study were to characterize the soils through their physical, chemical, and mineralogical properties, to deduce the processes of soil formation relative to hillslope position, and to classify the soils in the Brazilian Soil Classification System and in Soil Taxonomy and suggest revisions of these systems where necessary.

2. Soils studied

Soils with plinthite and ironstone occur in Maranhão State, Brazil (Fig. 1), under a tropical subhumid climate with strong seasonal dry/wet cycles. The mean annual air tem-

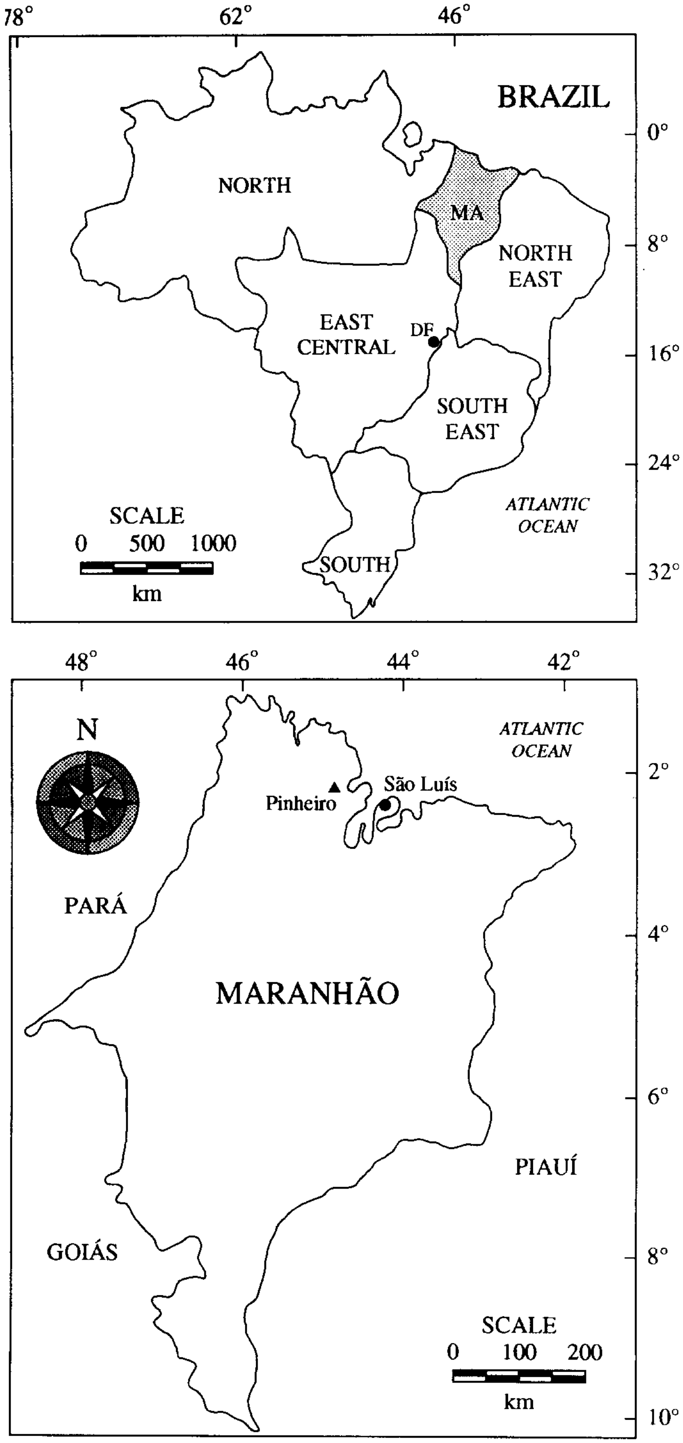

Fig. 1. Location of study area, near Pinheiro, Maranhão State, Brazil.

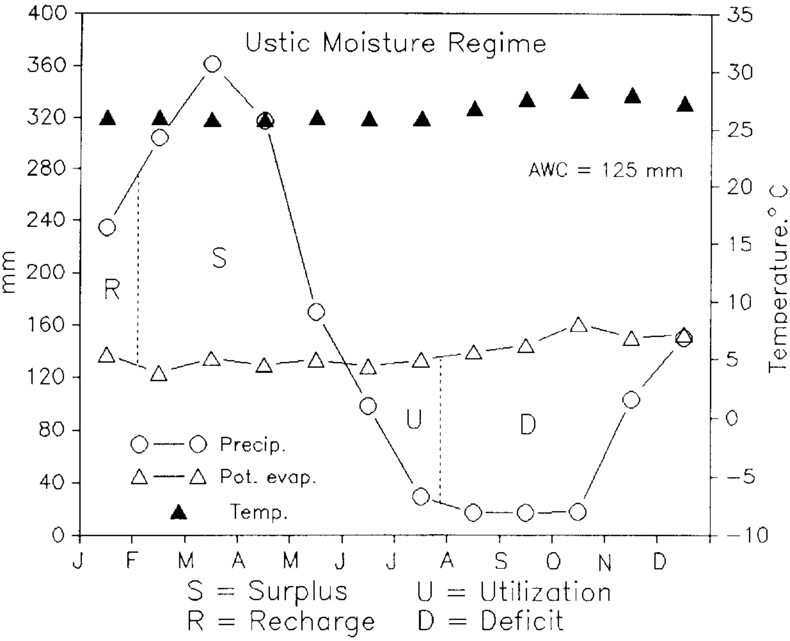

Fig. 2. Representative water balance for Pinheiro County, Maranhão State.

perature is 26°C, and the annual rainfall is 1800 mm (Fig. 2). According to the Köppen climatic classification, the area is type Aw′, with rainy summer and fall and dry winter (EMBRAPA, 1986). The upland areas are partially covered by the original vegetation of semi-deciduous tropical broadleaf forest. The secondary vegetation, which resulted from shifting cultivation, is characterized by palm-trees, locally called "babaçu" (*Orbignya* sp.) and "tucum" (*Astronum tucumoides*), and shrubs. The seasonally flooded plains are characterized by herbaceous species and are generally bordered by evergreen tropical forest with palm-trees. The parent rocks belong to the Lower Cretaceous Itapecurú Formation which consists of horizontally bedded, fine-grained sandstones interbedded with Fe-rich sandstone. In the general area, individual beds range from a few cm to 1 m in thickness. In the sampling area the two sandstones occur in about the same proportions and the strata vary from about 40 to 60 cm in thickness. The Fe-rich layers have relatively greater silt contents and the Fe-poor layers have greater fine sand contents. The soils formed from both kinds of rocks.

Other parent materials are unconsolidated colluvial or alluvial sediments derived from sandstone and deposited in the lower elevations of the landscape. The colluvium is sandy and not stratified, but often contains layers of ferruginous nodules or concretions.

Six soil profiles were selected for the study (Fig. 3). Profile 1 (P1) and P5 are on summit positions and are well drained. P4 and P6 are on shoulder positions and are moderately well drained. All four formed by in situ weathering of the sandstone. P2 and P3, on footslope positions and somewhat poorly or poorly drained, formed from sediments derived from the sandstone. Soils P2, P3, P4, and P6 had significant amounts of plinthite. All soils have an isohyperthermic soil temperature regime. The soils on uplands have an ustic moisture regime. The lower part of the landscape has alternating conditions of free drainage and high

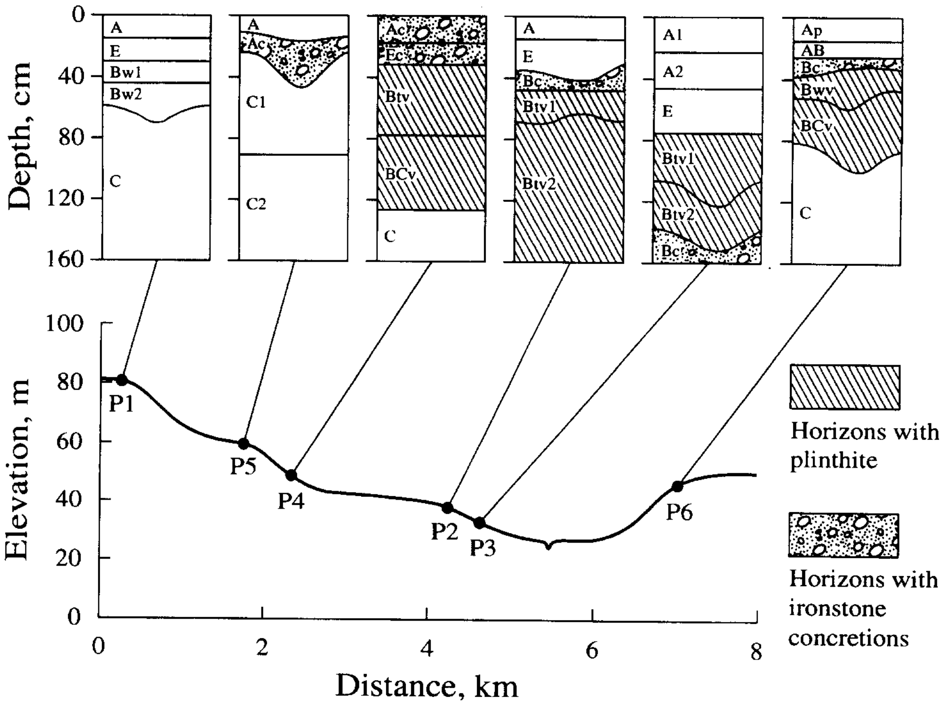

Fig. 3. Diagrammatic representation of soil profiles and their position in the landscape.

water table levels, and the soils in these positions have an aquic moisture regime (Soil Survey Staff, 1975).

3. Methods

3.1. Field methods

The six pedons were described and sampled according to standard procedures of the Soil Survey Manual (Soil Survey Staff, 1951, and unpublished updates). Samples of sandstone were collected from P1. Samples from both the plinthic material and the non-plinthic soil matrix were collected from the Btv2 horizon of P2. The existence of plinthite was verified by placing aggregates in water and observing them after they had been shaken gently for 2 hours. The material that did not slake with this treatment was considered to be plinthite (Wood and Perkins, 1976a,b; Daniels et al., 1978).

3.2. Laboratory methods

Soil characterization. Samples of the < 2 mm fraction were analyzed following standard soil survey characterization procedures (EMBRAPA, 1979). The soils were dispersed by adjusting the pH to 10–11 with 1N NaOH and then particle-size distribution was determined by the pipette method. Water-dispersible clay content was determined after dispersion in water only. The aggregation (flocculation) degree was calculated as 100 × (total clay − water-dispersible clay)/total clay. Samples were extracted with 1M KCl for Ca^{2+}, Mg^{2+}, and Al^{3+}, with 0.05M HCl and 0.025M H_2SO_4 for K^+ and Na^+, and with pH 7.0 1M $Ca(OAc)_2$ for extractable acidity $(H^+ + Al^{3+})$. Extractable $H^+ = (H^+ + Al^{3+})$ minus extractable Al^{3+}. The sum of bases is the sum of extractable Ca^{2+}, Mg^{2+}, K^+, and Na^+; the cation exchange capacity (CEC) is the sum of bases plus acidity; the base saturation (%) is (sum of bases/CEC) × 100; and Al saturation (%) is [ext. Al/(ext. Al + sum of bases)] × 100. Organic C was determined by wet oxidation with $K_2Cr_2O_7$. Soil samples were also extracted with strong H_2S0_4. A 2 g soil sample was boiled in 9M H_2SO_4 for 1 h, and Al, Fe, and Si in the extract were determined by volumetric and colorimetric methods.

Specific surface area was determined by the ethylene glycol monoethyl ether (EGME) technique (Carter et al. 1965; Heilman et al. 1965).

Dithionite–citrate–bicarbonate (DCB) extract. One extraction was done following the Holmgren (1967) modification of the Mehra and Jackson (1960) procedure. After the addition of dithionite–citrate–bicarbonate the samples were placed on a reciprocal shaker overnight at room temperature. Then, samples were centrifuged, filtered and washed. The Fe in the extracts (Fe_d) was determined by the colorimetric thiocyanate method (Aguilera and Jackson, 1953) and Al (Al_d) by atomic absorption spectroscopy.

Ammonium oxalate extraction. Twenty mL of 0.2 M oxalate–oxalic acid solution adjusted to pH 3.0 was added to 0.5 g soil, and the suspension was shaken for 2 hours in the dark (Schwertmann, 1964). The Fe in the extract (Fe_o) was determined by the colorimetric thiocyanate method.

Optical mineralogical analysis. Minerals in the sand and gravel fractions were identified according to Winchell and Winchell (1951) by optical microscopy.

X-ray diffraction. Samples of fine silt (2–5 μm), coarse clay (0.2–2 μm), and fine clay (< 0.2 μm) were separated using methods described by Jackson (1969). Organic matter and carbonates were removed with H_20_2 and NaOAc, respectively. The different soil fractions were separated by standard sieving (sand), sedimentation, and centrifugation techniques. The concentrated fractions of silt and clay were dialyzed against deionized water to remove excess electrolyte and then freeze-dried. Coarse clay and fine clay fractions were analyzed using oriented mounts with the following treatments: K-saturated 25°C, K-saturated heated to 300°C, K-saturated heated to 550°C, Mg-saturated, and Mg- and glycerol-saturated. The samples were step scanned from 2 to 36° 2θ using 0.02° steps and 1 s count times on a Philips 3100 generator (CoKα, 35 kV, 25 mA) with a Philips 3520 APD diffractometer. Silt and clay minerals were identified by comparison with standard values of diffraction peaks from the Mineral Powder Diffraction File.

Differential X-ray diffraction (DXRD). Samples of coarse clay and fine clay from subsurface horizons were treated for selective dissolution of iron oxides using the DCB procedure (Holmgren, 1967) and then X-rayed. Self-supporting powder mounts were prepared by back filling 100 to 150 mg of powder sample into an Al sample holder and gently pressing against uncoated paper. Both the DCB treated and untreated samples were step scanned from 12 to 60° 2θ using 0.05° steps and 20 s count times. DXRD diagrams were made as described by Schulze (1981, Schulze 1986).

Infrared spectroscopy. Samples of coarse and fine clay were gently ground in an agate mortar and a suspension (2 mg clay/ml deionized water) was pipetted onto AgCl infrared-transparent windows. Infrared absorption patterns were obtained using a Perkin Elmer, model 1600 FT-IR spectrophotometer.

Micromorphological methods. Soil samples were impregnated with epoxy resin under vacuum prior to making thin sections for examination with the polarizing microscope. Mineral grains or broken soil pieces were mounted on Al stubs with double-face tape, coated with a layer of gold-palladium, and examined with a JEOL JSM-840 high resolution scanning electron microscope (SEM) at the Electron Microscope Center, Purdue University. For transmission electron microscopy (TEM), an aliquot of clay was ultrasonically dispersed, and a small aliquot was placed on a carbon–Formvar-coated grid and examined with a Philips EM-200 instrument.

4. Results and discussion

4.1. Soil morphology

Soil color, natural drainage, depth of solum and plinthic features are the major characteristics separating the soil classes in the field. Soils P1 and P5, on small summit positions (Fig. 3), are well drained, have shallow sola, brownish colors, and contain rock fragments (Table 1). Soils P2 and P3, on footslopes, are somewhat poorly and poorly drained, respectively, have the deepest sola, neutral or gray colors in the subsurface horizons, and development of plinthite (v in horizon designations). Profiles P4 and P6, on shoulders, are moderately well drained, have intermediate sola depth, concretionary horizons (c in horizon designations) above the plinthic horizon and better development of structure in the subsurface diagnostic horizon. Soils P4 and P6 are also redder than P2 and P3. The occurrence of low chroma colors (2 or less) in P4 and P6 is related to the sandstone and is not evidence of an aquic soil moisture regime or of the presence of a perched water table during the wettest months. Soils P2, P3 and P4 have a few weakly expressed clay skins.

Concretions occur at different depths in the soil profiles, according to landscape position. In P2, P4, and P6 the concretionary horizon is above the plinthic zone but in P3 it is below it (Table 1, Fig. 3). The concretionary bodies have irregular, platy, rounded or subangular blocky structure in a matrix of friable earth of loamy texture. The diameter of the concretions varies from small (2–5 mm) to large (> 60 mm). In cross section, the concretions consist of different color zones: a dusky red to red very hard inner layer, dark reddish brown and yellowish brown outer layer, and intermediate colors in isolated spots. The pattern of concretions within a horizon of these soils differs from the clusters of ferruginous material solidly joined in polygonal networks up to 20 cm across observed in highly eroded land-

Table 1
Morphological descriptions of the soils studied

Profile	Horizon[a]	Depth (cm)	Color (moist)	Texture[a]	Structure[a]	Boundary[a]	Comments
Soils on summit positions							
P1	A	0–13	10YR 3/3	sl	1f–mgr	cs	
	E	13–26	10YR 4/4	sl	1fgr	cs	
	Bw1	26–42	10YR 4/6	scl	2msk	cs	mottles
	Bw2	42–57	7.5YR 4/2	sl	2msk	gw	mottles
P5	A	0–9	10YR 3/1	sl	2mgr	cw	
	Ac	9–25	10YR 3/2	sl	1fgr–sbk	ci	28% gravel
	C1	25–92	mottled[b]	sl	massive	cs	stratified
	C2	92–126	mottled	sl	massive	–	weath. rock
Soils on shoulder positions							
P4	Ac	0–20	10YR 4/3	sl	1fgr	gs	56% gravel
	Ec	20–34	10YR 5/3	scl	massive	as	59% gravel
	Btv	34–79	7.5YR 5/2	cl	3f–msk	gw	mottles
	BCv	79–125	N 5/	l	2msk	gs	mottles
	C	125–132	weathered sandstone				
P6	Ap	0–12	10YR 3/3	sl	1f–mgr	cs	
	AB	12–27	10YR 5/4	l	1fgr	as	
	Bc	27–32	10YR 6/4	l	1msbk–sk	aw	18% gravel
	Bwv	32–46	10YR 6/6	l	2msbk–sk	ci	mottles
	BCv	46–80	mottled	sl	massive	cw	
	C	80–126	mottled	l	massive		
Soils on footslope positions							
P2	A	0–17	10YR 4/2	ls	1f–mgr	gs	
	E	17–36	10YR 6/1	sl	1fsbk	aw	
	Bc	36–53	10YR 6/1	scl	–	as	41% gravel
	Btv1	53–66	N 6/	scl	2msbk–sk	gw	mottles
	Btv2	66–128	N 6/	scl	2m–csk	–	mottles
P3	A1	0–28	10YR 4/3	ls	1f–mgr	cs	
	A2	26–46	10YR 5/3	ls	1fgr	gs	
	E	46–78	10YR 6/3	ls	massive	cs	
	Btv1	78–103	N 6/	sl	1fsbk	gw	mottles
	Btv2	103–139	10YR 6/1	scl	1msbk–sk	aw	mottles
	2Bc	139–164	–	scl	–	–	74% gravel

[a] Horizon designations and abbreviations as used in Soil Survey Staff (1951). The meanings of the lower-case letters in the horizon designations are: c – concretions; t – accumulation of silicate clay; v – plinthite; w – development of color or structure. [b] "Mottled" in the color column means that there is no predominant color.

scapes in other parts of the region (UFRRJ, 1986). The morphology of these Brazilian soils seems to be similar to those described by Nahon (1991) for tropical landscapes with alternating dry and rainy seasons.

4.2. Micromorphology

Thin sections show that plinthic material in the Bwv horizon of P6 is optically dense and has a sharp boundary with non-plinthic material (Fig. 4a). Cracks penetrate the plinthic

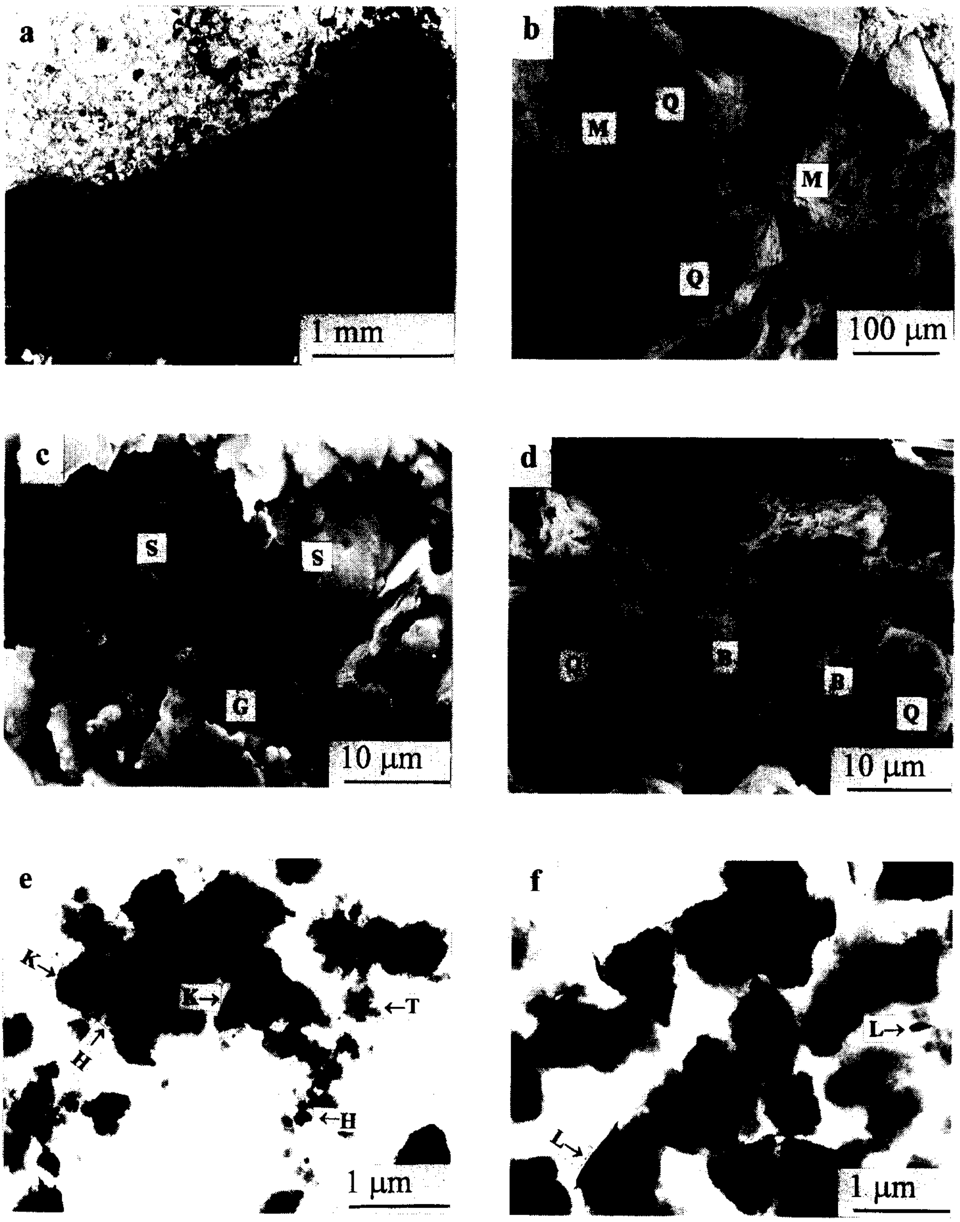

Fig. 4. Micrographs of soil features. (a) Thin section through the non-plinthic matrix (top) and plinthic material (bottom) of the Bwv horizon of P6 (ordinary light). (b) SEM of a broken surface of a ferruginous concretion from soil P2 showing a quartz grain (*Q*) embedded in fine-grain, Fe-rich material (*M*). (c) SEM of a broken surface of plinthite from the Btv2 horizon of P2 showing gelatinous material (*G*) draped over silt particles (*S*) and clay aggregates. (d) SEM of the 5–20 μm fraction from the Btv2 horizon of P2 showing mica "books" (*B*) and etched quartz grains (*Q*). (e) TEM of the coarse clay fraction (0.2–2 μm) of sandstone showing kaolinite (large electron-dense particles, *K*), 2:1 minerals (less dense material, *T*) and hematite (small, dense masses, *H*). (f) TEM of the coarse clay of the Btv2 horizon of P2; the lath shaped grains with serrated ends are lepidocrocite (*L*).

Table 2
Physical properties and organic carbon content of the soils

Profile	Horizon	Particle size (% of <2 mm)			Aggreg. degree[a]	Silt/Clay	Surface area (soil)	Organic C
		Sand	Silt	Clay	(%)		($m^2 g^{-1}$)	($g\ kg^{-1}$)
Soils on summit positions								
P1	A	75	15	10	30	1.50	35.4	11.5
	Bw1	64	15	21	14	0.71	105.3	3.7
	Bw2	67	16	17	18	0.94	122.6	2.3
P5	A	71	16	13	61	1.23	71.9	14.0
	C1	74	7	19	53	0.37	157.3	3.0
	C2	77	6	17	71	0.35	169.2	1.4
Soils on shoulder positions								
P4	Ac	64	21	15	60	1.40	51.4	16.5
	Btv	35	28	37	43	0.76	214.4	2.8
	BCv	36	37	27	41	1.37	222.7	2.1
P6	Ap	53	31	16	56	1.94	51.9	7.5
	Bwv	47	30	23	39	1.30	120.8	3.0
	BCv	62	20	18	44	1.11	122.3	1.7
Soils on footslope positions								
P2	A	81	9	10	10	0.90	45.7	4.1
	Btv1	67	9	24	12	0.37	136.4	2.3
	Btv2	62	14	24	17	0.58	168.2	2.1
	plinth.[b]	56	27	17	–	1.59	–	–
	n/plinth.[b]	59	14	27	–	0.52	–	–
P3	A1	80	9	11	36	0.82	30.0	4.3
	Btv1	75	9	16	6	0.56	73.1	1.7
	Btv2	66	12	22	14	0.54	123.5	1.6
Fe-Sandstone		3	59	38	–	1.55	222.9	–

[a] Aggregation degree is 100 × (total clay – water dispers. clay) / total clay.
[b] plinth.: plinthite body, and n/plinth.: nonplinthic soil matrix from Btv2.

material, and argillans cover the soil matrix surrounding the void. These argillans are dark reddish brown (ferriargillans) near the matrix and grade through yellowish brown to almost colorless near the planar void, which suggests that Fe probably was reduced and lost from this surface when the voids were filled with water. Occasional saturation is indicated by the redoximorphic features that were described in this moderately well drained soil. Higher magnification of a broken surface with SEM shows that in the hard ironstone concretions the space between grains is almost completely filled with plasmic material (Fig. 4b). In the softer plinthic material, however, gel-like material drapes over silt particles and clay aggregates but some small pores remain (Fig. 4c).

4.3. *Physical and chemical properties*

Clay content ranges from 16% (P3) to 37% (P4) in the subsurface horizons (Table 2). The silt/clay ratio is much higher for the plinthic material from P2 (Btv2) than for the

Table 3
Chemical properties

Profile	Horizon	pH (H_2O) (1:2.5)	($cmol_c\ kg^{-1}$) Sum bases	Ext. Al^{3+}	Ext. H^+	CEC sum	CEC clay[a]	Base sat. (%)	Al sat. (%)
Soils on summit positions									
P1	A	5.3	3.8	0.7	4.9	9.4	42.2	40	16
	Bw1	4.9	2.6	5.1	2.6	10.3	41.1	25	66
	Bw2	5.0	2.7	8.0	1.0	11.7	62.7	23	75
P5	A	4.0	1.3	3.4	4.3	9.0	20.8	14	72
	C1	5.1	2.3	9.0	0.2	11.5	53.4	20	80
	C2	5.1	2.7	9.8	0.6	13.1	73.4	21	78
Soils on shoulder positions									
P4	Ac	5.0	2.3	0.8	5.3	8.4	6.5	27	26
	Btv	5.0	2.2	5.3	1.6	9.1	21.5	24	71
	BCv	5.0	2.2	7.3	1.4	10.9	36.9	20	77
P6	Ap	5.6	2.1	1.1	3.6	6.8	21.4	31	34
	Bwv	5.1	3.4	3.3	2.4	9.1	33.7	37	49
	BCv	5.3	4.3	5.0	1.6	10.9	56.3	39	54
Soils on footslope positions									
P2	A	5.2	1.7	0.8	3.4	5.9	40.5	29	32
	Btv1	5.0	1.7	5.4	2.0	9.1	33.6	19	76
	Btv2	5.1	2.7	7.5	0.8	11.0	41.9	24	73
P3	A1	4.9	1.2	1.0	3.6	5.8	35.1	21	45
	Btv2	5.0	1.9	2.7	2.6	7.2	29.4	26	59

[a] $CEC_{clay} = [(CEC\ sum) - (4.5 \times \%C)] \times 100/\%clay$.

nonplinthic soil matrix in the same horizon which suggests that much of the clay in the plinthic horizon is in aggregates. In general, the two soils without plinthite, P1 and P5, had lower clay contents than the soils with plinthic horizons, P2, P3, P4, and P6. For the plinthic soils, the poorly drained ones, P2 and P3, had the lowest aggregation degree and silt/clay ratio. Specific surface areas of subsurface horizons are higher than in other soils with plinthite reported in the literature. Soils P2 and P3, on lower landscape positions, have the lowest levels of organic C in surface horizons (Table 2).

The pH determined in water (Table 3) ranges from 4.0 to 5.6, and base saturation is <50% for all soils. The dominant base cations are Ca and Mg, with levels of Mg > Ca for most horizons (data not shown). Al saturation is high, especially in well drained soils such as P5. The CEC of the total clay fraction was calculated from the CEC for the whole soil, the clay content, and an allowance for the CEC of organic matter (footnote Table 3). The CEC of clay from subsurface horizons ranges from 21 (P4) to 73 (P5) $cmol_c\ kg^{-1}$, while most Plinthosols in Brazil have $< 24\ cmol_c\ kg^{-1}$. For reference, the oxic and kandic horizons of Soil Taxonomy, which are characterized by low-activity clays, have $< 16\ cmol_c\ kg^{-1}$ of clay (Soil Survey Staff, 1992).

Strong H_2SO_4 dissolves most of the clay fraction, so the Fe in the extract approximates the total Fe content of the clay fraction and is designated Fe_t. DCB extracts mainly Fe-

Table 4
Chemical composition of soils and Fe-rich sandstone

Profile	Horizon	H_2SO_4 [a]			DCB [a]		Oxal. [a] Fe (Fe_o)	Fe_d/clay	Fe_o/Fe_d	$Al_d/(Fe_d)$
		Si	Al	Fe (Fe_t)	Fe (Fe_d)	Al (Al_d)				
Soils on summit positions										
P1	A	27	17	6	2.1	0.49	0.5	0.02	0.23	0.23
	Bw1	52	26	10	6.6	1.05	0.8	0.03	0.12	0.16
	Bw2	53	35	13	6.2	1.21	0.8	0.04	0.13	0.20
P5	A	39	25	6	2.9	0.81	0.9	0.02	0.31	0.28
	C1	63	44	11	4.1	1.70	0.2	0.02	0.05	0.41
	C2	59	35	11	4.2	1.56	0.1	0.02	0.02	0.37
Soils on shoulder positions										
P4	Ac	31	21	18	5.1	0.76	1.0	0.03	0.20	0.15
	Btv	84	66	35	13.8	1.62	0.9	0.03	0.07	0.12
	BCv	92	66	24	9.3	1.70	0.5	0.03	0.05	0.18
P6	Ap	36	21	7	3.4	0.57	1.4	0.02	0.41	0.17
	Bwv	67	44	27	9.3	0.86	0.8	0.04	0.09	0.09
	BCv	79	55	22	7.8	0.97	0.6	0.04	0.08	0.12
Soils on footslope positions										
P2	A	26	20	5	3.1	0.46	0.6	0.03	0.19	0.15
	Btv1	58	41	11	8.4	1.16	0.9	0.04	0.11	0.14
	Btv2	72	54	12	9.0	1.30	0.6	0.04	0.07	0.14
	pl[b]	47	40	25	23.2	6.99	1.0	0.14	0.04	0.30
	n/pl[b]	57	48	13	4.9	2.59	0.6	0.02	0.12	0.53
	Cncr.	35	41	269	187.0	10.01	0.2	–	<0.01	0.05
P3	A1	21	13	5	2.1	0.49	0.6	0.02	0.29	0.23
	Btv1	36	20	9	5.6	0.54	0.6	0.04	0.11	0.10
	Btv2	51	38	16	9.3	0.70	0.5	0.04	0.05	0.08
Fe-Sandst.		90	58	48	32.0	2.99	0.1	0.09	<0.01	0.09

[a] Values in g kg^{-1}
[b] pl: plinthite body, and n/pl: nonplinthic soil matrix from Btv2.

oxides and is designated Fe_d. Both Fe_t and Fe_d are much higher in the Fe-rich layer of the sandstone parent material than in the soils (Table 4), suggesting that Fe is lost during soil formation. Among the soils, Fe_t contents are highest in P4 and P6, on shoulder positions. Fe_d contents are highest on shoulders, intermediate on footslopes, and lowest on summits. Within soils, however, the greatest concentrations of Fe are in plinthite and concretions, as shown by Fe_t and Fe_d in these materials compared to other soil materials (Table 4). The concretions have higher Fe contents than the sandstone parent material. The Fe_d content in the plinthic sample (P2, Btv2) was about five times greater than the nonplinthic soil matrix. Similar results have been reported by Perkins and Lawrence (1982). The Fe_o/Fe_d ratio in plinthite is relatively low. For example, it is 0.04 in plinthic material and 0.12 in nonplinthic material in soil P2. The smallest Fe_o/Fe_d ratios were observed for the Fe-rich sandstone, and concretions from P2 (Table 4). Low Fe_o/Fe_d ratios indicate that the Fe is well crystallized. Fe_t and Fe_d contents are much greater in subsoil horizons than in surface horizons, which indicates that Fe has moved downward in the soil profile. The Fe_d/clay ratio increases slightly from surface to subsoil horizons for most of the soil profiles, except for P4 and P5 where it is uniform throughout the sola (Table 4). Uniform ratios indicate that soil clay and Fe oxide move together (Blume and Schwertmann, 1969). However, for the plinthite sample (17% clay) and the nonplinthic soil matrix (27% clay) from P2, the Fe_d/clay ratios are 0.14 and 0.02 respectively, indicating segregation of iron oxides from the soil matrix during plinthite formation.

Chemical data from soil horizons that contain plinthite or concretions (v or c in the horizon designation) were compared with data from those that lack these materials to find criteria that could be used to make this separation. The criterion that plinthic horizons contain >9 g kg^{-1} Fe_t correctly placed 17 of the 20 horizons (data for some of the horizons considered are not presented here). A Fe_d content of >3.5 g kg^{-1} in plinthic horizons correctly placed 18 samples, and a Fe_o/Fe_d ratio of <0.11 in plinthic horizons correctly placed 17 samples. These relationships confirm that plinthic horizons are high in total Fe and in Fe oxides relative to other horizons of these soils, and that most of these oxides are crystalline.

4.4. *Gravel and sand mineralogy*

The gravel fraction is dominated by hematitic and goethitic ferruginous concretions with inclusions of clear quartz grains in the matrix. Few individual quartz grains occur in this large fraction.

The sand fractions of the sandstone and most soil horizons are dominated by subangular quartz grains and other weathering-resistant minerals such as ilmenite, rutile, tourmaline, and zircon. Quartz grains are mainly colorless, but some have yellowish and reddish opaque surfaces. The sand fractions also contain ferruginous concretions, fragments of coarse material, clay aggregates, muscovite, weathered K-feldspar (microcline) and weathered biotite. Muscovite occurs as platy, colorless, very thin flakes. The weathered sand grains indicate only moderate weathering of these soils. Comparison of samples from the Btv2 horizon, P2, showed a greater content of clay aggregates and ferruginous concretions in the plinthic than in the nonplinthic material. The pattern of concretions within a horizon of these soils differs from the clusters of ferruginous material solidly joined in polygonal networks up to 20 cm across observed in highly eroded landscapes in other parts of the region (UFRRJ, 1986). The amounts of muscovite and weathered mica, weathered feldspar, and resistant minerals are similar in the sand fractions of both samples. The differences observed are related to the accumulation of iron in the plinthite sample. This horizon has some rounded quartz grains.

4.5. *Silt and clay mineralogy*

Mineral grains in the medium silt range (5–20 μm) of soils are mainly quartz and weathered mica "books" (Fig. 4d). According to XRD (Figs. 5 and 6), the coarse clay fractions (0.2–2 μm) of the Fe-rich layer of sandstone and the subsurface horizons of the six soil profiles contain kaolinite (7.2, 3.59 Å), smectite (18 Å), mica (10 Å), and lepidocrocite (6.27 Å). The original XRD diagrams also show peaks for quartz (4.26, 3.34

Å), rutile (3.25 Å), and anatase (3.52 Å). Higher order peaks, (002) = 9.10 Å and (003) = 6.31 Å, were observed for smectite in subsurface horizons of P1, P2, P3 and P5. The fine clay fraction (< 0.2 μm) contains kaolinite, smectite, and, in some horizons, mica.

The relative amount of the various clay minerals identified by X-ray diffraction was estimated by measuring the area under the first-order diffraction peak of each mineral (Table 5). Except for P5, kaolinite is the most abundant mineral in the coarse clay fraction of the

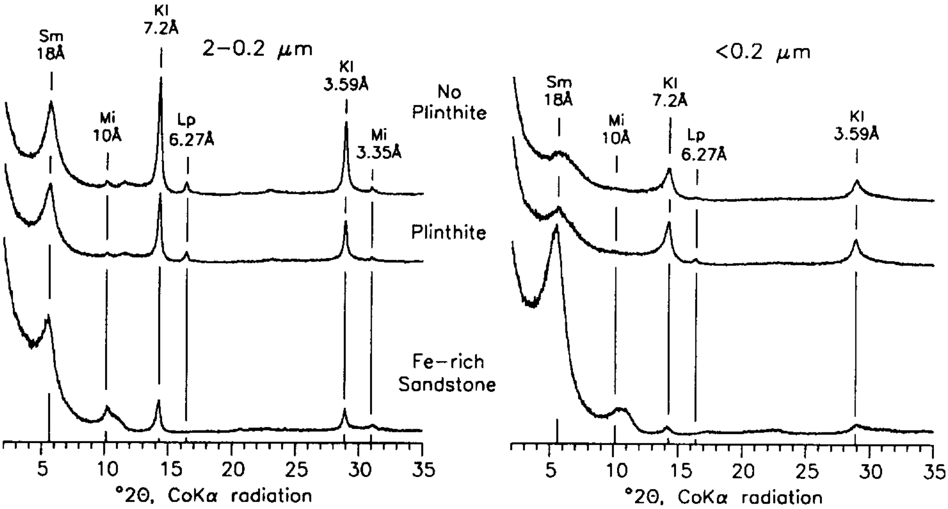

Fig. 5. X-ray diffraction patterns of oriented, Mg + glycerol saturated samples of clay fractions from the plinthic and non-plinthic material of the Btv2 horizon of P2, and Fe-rich sandstone.

Table 5
Relative amounts[a] of silicate minerals in the clay fraction.

Pedon, Horizon	Coarse clay				Fine clay			
	Sm[b]	Kl	Mi	Qtz	Sm	Kl	Mi	Qtz
Soils on summit positions								
P1, Bw1	2	3	1	1	2	1	0	0
P5, C2	3	1	1	1	3	1	0	0
Soils on shoulder positions								
P4, Btv	1	2	1	1	1	2	0	0
P6, Bwv	1	1	1	1	0	1	1	0
Soils on footslope positions								
P2, Btv2	2	2	1	1	2	2	0	0
Plinthite	2	2	1	1	2	2	0	0
No plinthite	2	3	1	1	2	2	0	0
P3, Btv2	1	3	1	1	1	2	0	0
Sandstone	2	1	2	1	3	1	2	0

[a] Relative amounts: 0 – Not detected, 1 – Present, 2 – Moderately abundant, 3 – Abundant.
[b] Sm – Smectite; Kl – Kaolinite; Mi – Mica; Qtz – Quartz.

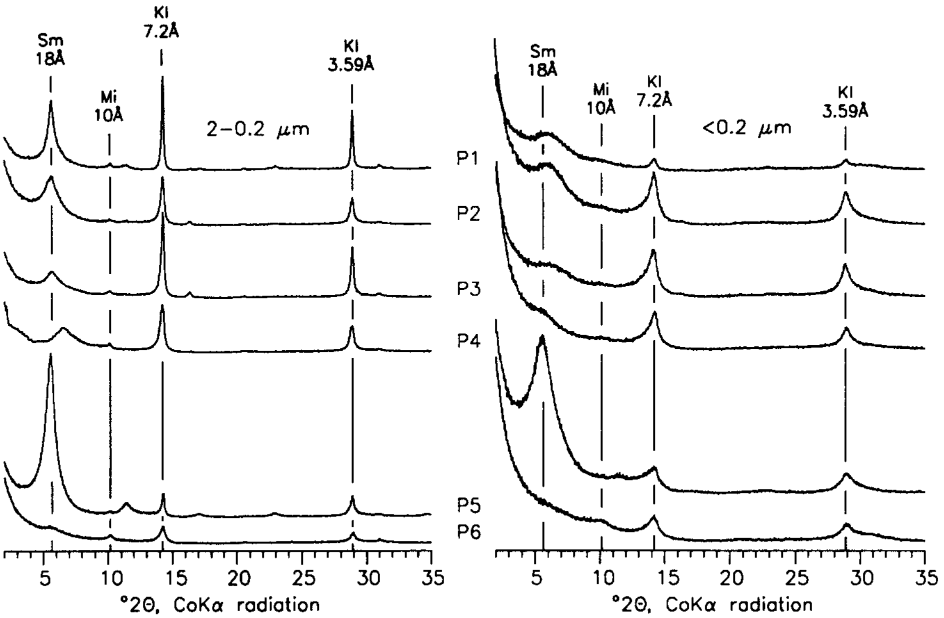

Fig. 6. X-ray diffraction patterns of oriented, Mg + glycerol saturated samples of clay fractions from the major B horizons of six soils.

subsoil horizons. Appreciable amounts of expanding clay and some quartz were found in the coarse clay. Generally, the mica level is relatively constant or increases slightly with depth. This distribution indicates a weathering status not as advanced as usually thought necessary for plinthite formation. Gibbsite was not detected in the X-ray patterns from the oriented samples. The coarse and fine clay from the Fe-rich sandstone is relatively high in smectite and mica (Fig. 5, Table 5). Smectite was also abundant in the C2 horizon of P5 (Fig. 6). Relative to these parent materials (sandstone and C2 horizon), the B horizons were lower in smectite and mica content and higher in kaolinite content. Apparently the 2:1 minerals have weathered to kaolinite in these soils.

Among the soils, smectite content was high in P5, intermediate in P1 and P2, and low in P3, P4 and P6 (Fig. 6, Table 5). Horizons with high smectite contents also had clay fractions with relatively high CEC values (Table 3). Well defined diffraction peaks for kaolinite and smectite were observed in the plinthic and nonplinthic materials from P2. In general, for the coarse clay, the diffraction peaks for the plinthic material were lower in intensity than those for the non-plinthic material (Fig. 5), but there is no difference in the mineralogical composition of the two materials.

Most smectite in P1 and P5 was probably inherited from the parent material. In P2, a somewhat poorly drained soil, the footslope position would favor the accumulation of bases as well as Si, favorable for the formation of smectite. Profile 3, even though it is located on the footslope and is poorly drained, has a sandier texture than P2, resulting in more intensive leaching of bases favoring kaolinite formation. It also has a different parent material, alluvial sediments. Kaolinite formation is favored in P4 and P6 on shoulder landscape positions. The absence of gibbsite is an indicator of the relatively low degree of weathering of the

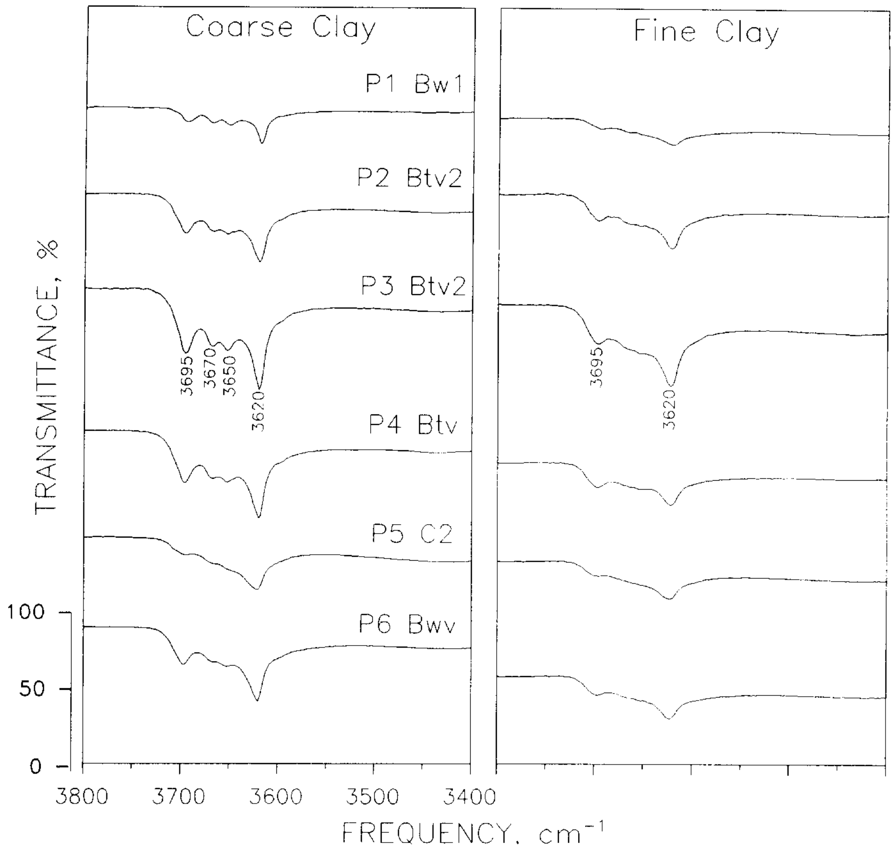

Fig. 7. Infrared spectra of coarse clay (0.2–2 μm) and fine clay (< 0.2 μm) from major subsoil horizons of six soils.

soils formed from sandstone. These soils have high contents of fine sand which can release enough Si into solution to inhibit gibbsite formation.

In the micrographs of the coarse clay (0.2–2 μm) of the sandstone sample (Fig. 4e), the large electron-dense particles and others with 120° angles are probably kaolinite. The less dense material consists of 2:1 minerals, probably mica or smectite, and the small dense masses appear to be hematite. The coarse clay in a horizon with plinthic material contains mainly kaolinite, 2:1 minerals, and lepidocrocite — the lath-shaped grains with serrated edges (Fig. 4f).

Well crystallized kaolinite was identified in the coarse clay fraction of B horizons by the four well defined OH-stretching bands at about 3695, 3670, 3650 and 3620 cm^{-1}. For P5 (C horizon), only the 3695 and the 3620 cm^{-1} bands are well differentiated (Fig. 7). In general, the infrared spectra show a higher intensity of kaolinite bands for P2, P3, and P4, than for P1, P5, and P6. In the fine clay, only the 3695 and 3620 cm^{-1} bands are well expressed, indicating poor crystallization of kaolinite (Dixon, 1989). Other IR bands confirmed the XRD identification of smectite and the lack of gibbsite.

4.6. *Fe-oxide mineralogy*

The content of all Fe-oxide minerals in a sample is represented by the Fe$_d$ value in Table 4, and the distribution of the oxides according to kinds of minerals is represented by the

Table 6
Relative amounts[a] of Fe-oxide minerals in the clay fraction

Pedon, Horizon	Coarse clay			Fine clay		
	Hm[b]	Gt	Lp	Hm	Gt	Lp
Soils on summit positions						
P1, Bw1	0	0	1	0	1	0
P5, C2	0	1	1	0	1	0
Soils on shoulder positions						
P4, Btv	0	2	0	0	2	0
P6, Bwv	0	1	1	0	1	0
Soils on footslope positions						
P2, Btv2	0	1	1	0	1	1
Plinthite	1	1	2	1	1	2
No plinthite	0	1	1	0	1	1
P3, Btv2	0	1	1	0	0	1
Sandstone	3	0	0	3	0	0

[a] Relative amounts: 0 – Not detected, 1 – Present, 2 – Moderately abundant, 3 – Abundant.
[b] Hm – Hematite; Gt – Goethite; Lp – Lepidocrocite.

size of the DXRD peaks. These factors were used to derive Table 6, which lists the relative amount of Fe-oxide minerals in selected horizons. It should be noted that the Fe_d content of most soil horizons is less than 10 g kg^{-1}, so the term "moderately abundant" means that the mineral is significant relative to other Fe-oxide minerals, but represents only a small fraction of the whole soil. Small quantities of Fe-oxides, however, have a large influence on soil color and other properties related to their high specific surface area.

Hematite, the only Fe oxide in the Fe-rich sandstone (Table 6), is visible in TEM (Fig. 4e). Its (104) diffraction line, at 2.69 Å, is broader than the (110) line at 2.51 Å, indicating particles that are thinner along the *c*-axis than along the *a*-axis (Fig. 8). In soil horizons, hematite was identified only in the plinthite nodules of P2, where it was present in low concentration (Table 6).

Goethite and lepidocrocite (Fig. 4f) are the dominant Fe-oxide minerals in the soils. Goethite was identified by the (110) line at 4.18 Å and the (130) line at 2.69 Å, and lepidocrocite, by the (020) line at 6.27 Å and the (021) line at 3.30 Å (Figs. 8 and 9). Peak positions in goethite are shifted toward lower *d* spacings, indicating a substitution of Al for Fe in the goethite structure (Schulze, 1984). Compared with the non-plinthic matrix material, plinthic material contains more lepidocrocite and hematite (Table 6), and the Fe-oxides are better crystallized as indicated by the low Fe_o/Fe_d ratio (Table 4). The crystallinity relationship is in agreement with the results of Daugherty and Arnold (1982).

Fe-oxide mineralogy is related to hillslope position. Lepidocrocite is dominant in the soils on footslope positions (P2 and P3) where reductomorphic conditions prevail (Schwertmann and Taylor, 1989). Goethite dominates in soils on the better-drained shoulder positions (P4 and P6) in which oxidizing conditions prevail. In these soils, much of the Si released from the weathering of aluminosilicates is leached, and much of the Al substitutes

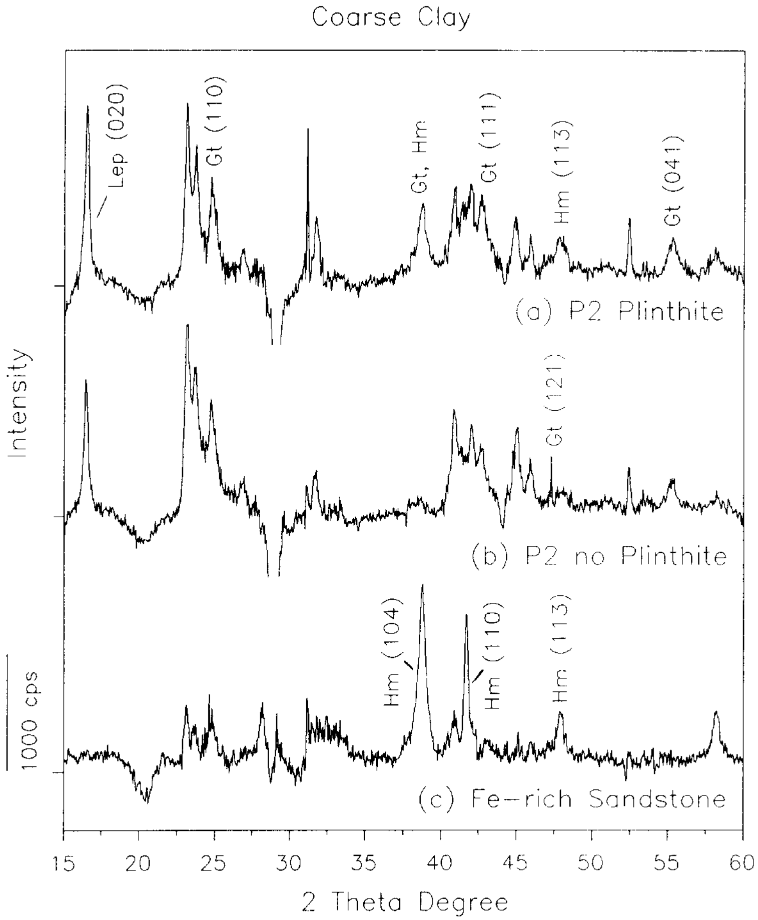

Fig. 8. DXRD patterns of coarse clay (0.2–2 μm) of (a) plinthic material and (b) non-plinthic material from the Btv2 horizon of P2, and (c) Fe-rich sandstone.

for Fe in Fe-oxide minerals. This factor, along with low pH, favors the formation of goethite over hematite, as reported by Kämpf and Schwertmann (1983) and Schwertmann and Taylor (1989). Soils on summits have a mineralogy intermediate between those on shoulders and those on footslopes.

Bigham et al. (1991) noted that associations of goethite and hematite and of goethite and lepidocrocite are frequently observed in soils, but the coexistence of lepidocrocite, goethite, and hematite has rarely been observed. In these soils hematite and lepidocrocite do not coexist in the same horizon except for the plinthite of P2 (Table 6). The amount of hematite in that material is very low (Fig. 8), and it could have been inherited from the parent rock.

4.7. Soil forming processes

Various soil forming processes take place in all soils but their intensities vary with hillslope position. The main minerals in the parent rock are quartz, other resistant minerals,

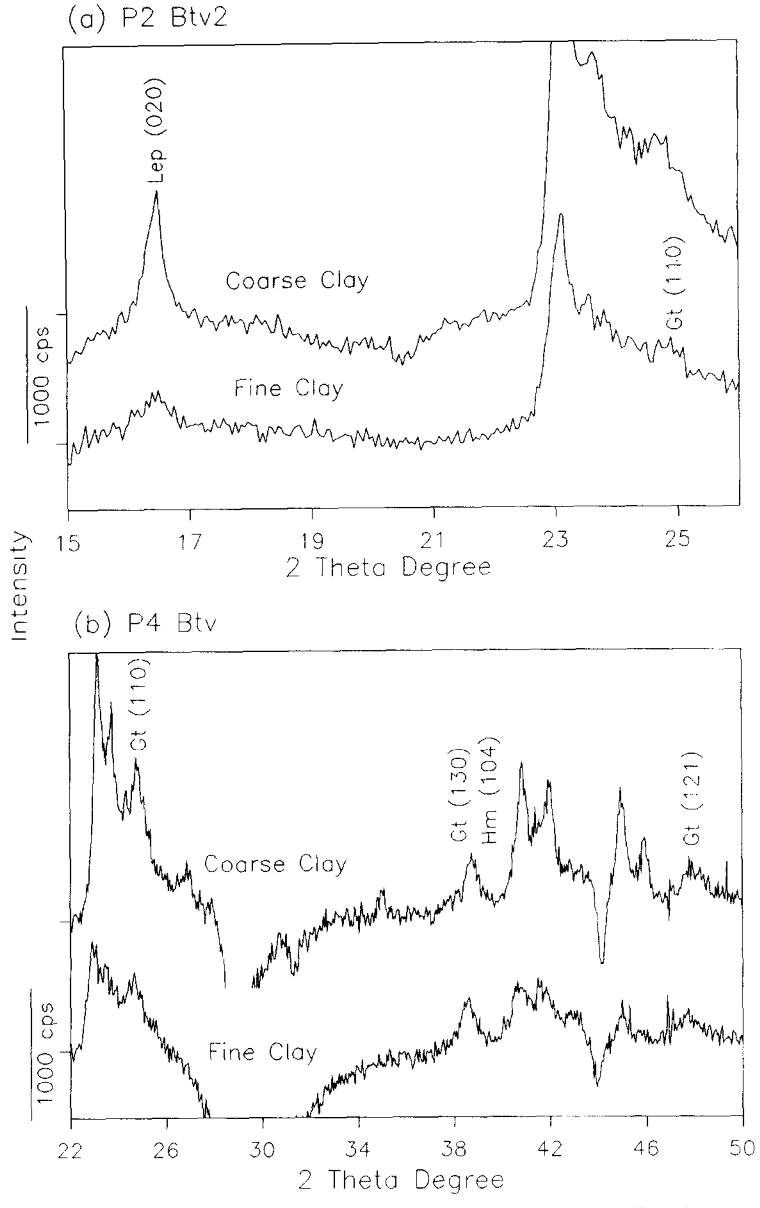

Fig. 9. DXRD patterns of coarse clay (0.2–2 μm) and fine clay (< 0.2 μm) from the Btv2 horizon of P2 and the Btv horizon of P4.

muscovite, biotite, and feldspars in the sand fraction, and smectite, mica, and kaolinite in the clay fraction. Hematite is essentially the only Fe-oxide mineral in the rock. Mineral weathering is generally intense in these acid soils with a warm environment, but the loss of silica from silicate minerals is countered by its release from the fine sand of the sandstone parent rock. Also, the weathering intensity varies with the moisture regime characteristic of the different landscape positions. In the soils, kaolinite and some 2:1 expandable minerals predominate. Apparently muscovite, biotite and feldspars weathered mainly to kaolinite. Soil smectite could be inherited or it could form in some soils such as those on footslopes that would receive additions of silica, Ca^{2+}, Mg^{2+}, and other cations. Hematite, and some silicate minerals, weathered and released Fe which precipitated to form goethite and lepidocrocite. The transformation of hematite to goethite and lepicocrocite must have proceeded through a solution phase according to Schwertmann and Taylor (1989). Mainly goethite formed in the moderately well drained soils on shoulders, and mainly lepidocrocite formed in the somewhat poorly drained soils on footslopes. These minerals probably formed during the present, more humid, climate, but it is possible that the climate was dryer during the Quaternary Period.

Fe, and other weathering products, can move between pedons in the landscape, between horizons in a pedon, within horizons, and entirely out of the soil–landscape. Apparently all soils showed a net loss of Fe because all soil horizons had a much lower Fe content than the sandstone parent material. Within the landscape it appears that Fe is most abundant in the soils on shoulders, moderately abundant in soils on footslopes, and least abundant in soils on summits. Fe also moves from upper to lower horizons within a pedon.

The most striking concentration of Fe, however, is in plinthite and ironstone concretions where its concentration is much higher than in the surrounding soil fabric and in the sandstone parent material. In most soils (P2, P4, and P6, Fig. 6) layers with ironstone concretions are *above* the plinthic zone. The study area has distinct wet and dry periods and in these somewhat poorly and moderately well drained soils the plinthic zone is periodically saturated with water. During periods of saturation, Fe is reduced and moves short distances to form zones of Fe depletion and Fe accumulation (gray and red mottles, respectively). During the dry season, Fe precipitates and cyrstallizes in the red mottles, weakly cementing them as plinthite. When these layers become better drained, such as when the water table is lowered through dissection of the landscape, the accumulation masses dry further, the Fe minerals become better crystallized, and the plinthite hardens further into ironstone concretions. The change in crystallization is documented by the Fe_o/Fe_d ratio which decreases with better crystallization In the Btv2 horizon of P2 the ratio is 0.12 in the non-plinthic material, 0.04 in plinthite, and <0.01 in ironstone concretions (Table 4). As erosion removes upper soil layers the concretionary layers become nearer the surface. At the same time, soil formation processes invade the parent rock, releasing Fe and clay minerals.

The concretionary layer was *below* the plinthic layer in one soil lower in the landscape (P3). Here plinthite probably formed in material deposited more recently on top of the concretionary layer.

4.8. Soil classification

Classification of the soils in the US and Brazilian systems (EMBRAPA, 1988) is presented in Table 7. Soils P1, P2, P3, and P5 were placed in existing Soil Taxonomy classes, but P4 and P6 could not be classified using current criteria.

In the current Keys to Soil Taxonomy (Soil Survey Staff, 1992) no subgroups of the Plinthustult great group are defined. Therefore a new class, *Inceptic Plinthustults* is proposed for soils such as P4. The Inceptic subgroup is proposed for Plinthustults that have the lower boundary of the argillic horizon within a depth of 125 cm of the soil surface. Other

Table 7
Classification of the soils

Profile	System of classification	
	Brazilian[1]	Keys to Soil Taxonomy[2]
P1	High-activity clay, allic (epidystrophic), moderate A, medium texture, Cambisols	Loamy, mixed, isohyperthermic Ustic Dystropepts
P2	High-activity clay, allic (epidystrophic), weak A, medium texture, endoconcretionary, Plinthosols	Loamy, mixed, isohyperthermic Typic Plinthaquults
P3	High-activity clay, allic (epidystrophic), weak A, medium texture, Plinthosols	Loamy, mixed, isohyperthermic Plinthis Paleaquults
P4	Low-activity clay, allic (epidystrophic), moderate A, clayey texture, epiconcretionary Plinthosols	Loamy-skeletal over clayey, mixed, isohyperthermic Inceptic Plinthustults
P5	High activity clay, allic, moderate A, medium texture, Lithosolic soil	Loamy, mixed, isohyperthermic Typic Ustorthents
P6	High activity clay, allic (epidystrophic), moderate A, medium texture, Cambisols, intermediate to endoconcretionary Plinthosols	Loamy, mixed, isohyperthermic Plinthic Dystropepts

[1] EMBRAPA (1988)
[2] Soil Survey Staff (1992).

Plinthustults would be in the Typic subgroup. The definition of the Inceptic subgroup is analogous to the concept of the class Inceptic Haplustox in the Keys to Soil Taxonomy (Soil Survey Staff, 1992). This soil would classify in the loamy-skeletal over clayey, mixed, isohyperthermic family. In the Brazilian system the following new class is proposed: Low-activity clay, allic (epidystrophic), moderate A, clayey texture, epiconcretionary Plinthosols.

Another new class, *Plinthic Dystropepts*, is proposed for P6. The subgroup Plinthic is proposed for Dystropepts that have 5% or more plinthite (by volume) in one or more subhorizon that is > 10 cm thick and has its upper boundary within 125 cm of the soil surface. This soil is in the loamy, mixed, isohyperthermic family. In the Brazilian system the following new class is proposed: High-activity clay, allic (epidystrophic), moderate A, medium texture, Cambisols intermediate to endoconcretionary Plinthosols.

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