

Lateral loss of clay in the genesis of Luvisols in the Semi-Arid Depression of the Jequitinhonha Valley, Minas Gerais – Brazil

Perda lateral de argila na gênese de Luvissolos na Depressão Semiárida do Vale do Jequitinhonha, Minas Gerais – Brasil

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ABSTRACT

Soils of the semi-arid region of Minas Gerais have small depth; hard, very hard or even extremely hard consistency when dry and very plastic and very sticky when moist; columnar or angular blocky structure and significant cracking along the profile in the dry period, however they have not been deeply studied yet. Thus, the aim of this study was to detail the genesis of Luvisols in the Semi-arid Depression of the Jequitinhonha Valley (MG), incompassing morphological, physical, chemical, micromorphological and mineralogical attributes, and their relationships. The lack of illuviation coatings in the micromorphological analysis is in line with the expressionless and unclear clay skins observed in the top of the B horizon in only one out of the four soil profiles during the field work. Considering the occurrence of expandable 2:1 clay minerals, which can easily modify such pedological feature, caution is recommended in relation to soil genesis interpretation. The lateral loss of the clay fraction from the superficial horizons is highlighted as the main formation process of the Luvisols studied. The cation exchange capacity of these soils revealed remarkable lower values for the Luvisols in semi-arid Brazilian regions.

Index terms: Soil mineralogy; cation exchange capacity; soil micromorphology.

RESUMO

Os solos da região semi-árida de Minas Gerais possuem pequena profundidade; consistência dura, muito dura ou mesmo extremamente dura quando seca e muito plástica e muito pegajosa quando úmida; estrutura colunar ou em blocos angulares e fendilhamento significativo ao longo do perfil no período seco, entretanto eles não foram profundamente estudados até agora. Assim, o objetivo deste estudo foi detalhar a gênese dos Luvissolos da Depressão Semi-árida do Vale do Jequitinhonha (MG), a partir de atributos morfológicos, físicos, químicos, micromorfológicos e mineralógicos, e suas relações. A ausência de cutãs de iluviação na análise micromorfológica em laboratório foi consistente com a fraca e pouca cerosidade observada no topo do horizonte B de apenas um dos quatro perfis de solo estudados durante os trabalhos de campo. Considerando a ocorrência de argilominerais 2:1 expansíveis, os quais podem facilmente modificar tal feição pedológica, cautela é recomendada com relação à interpretação da gênese do solo. Desta maneira, a perda lateral de argila dos horizontes superficiais é enfatizada como o principal processo de formação dos Luvissolos estudados. A capacidade de troca de cátions desses solos revelou valores diferencialmente mais baixos para Luvissolos em regiões semi-áridas brasileiras.

Termos para indexação: Soil mineralogy; cation exchange capacity; soil micromorphology.

INTRODUCTION

The Brazilian semi-arid region, which includes a part of the Jequitinhonha Valley, occupies an area of 980,000 km², corresponding to 11.5% of the Brazilian territory. The region is characterized by low rainfall that is poorly distributed, with long dry periods, and high mean temperatures. This set of climatic conditions produces soils with chemical, physical, morphological, and mineralogical characteristics that differentiate them from soils of hot and humid tropical regions of the country. These soils are generally less pedogenetically evolved, with low biological activity. Soils with a weak moderate A horizon predominate, which may be eutrophic or dystrophic, with or without salt accumulation (Araújo Filho et al., 2017; Jacomine, 1996). In Minas Gerais, most of the semi-arid region is located in the north of the state, occupying 17% of its territory.

The Luvisols occur only in the extreme northeast of Minas Gerais, near the border with the state of Bahia, and occupy an area of 1088 km² (Araújo Filho et al., 2017; CETEC, 1980; UFV-CETEC-UFLA-FEAM, 2010). These soils are found in the deciduous tropical forest domain, where they are extensively used for livestock raising, as in the municipalities of Jequitinhonha, Almenara, Salto da Divisa, Jacinto, and Jordânia, for example (Cetec, 1980; UFV-CETEC-UFLA-FEAM, 2010). Some soils of the semi-arid region of Minas Gerais have a shallow solum (A + B less than 100 cm); hard, very hard, or even extremely hard consistency when dry, but very plastic and very sticky when wet; and a structure that is columnar or in angular blocks, with expressive cracks throughout the profile in the dry period. These features are mostly related to the mineralogy of the clay fraction, which contains clay minerals of the smectite group. These soils tend to have high Na⁺ and Mg²⁺ contents and are normally solodic or sodic (Cetec, 1980; Brasil, 1987).

Although common in the semi-arid region of the Northeast of Brazil, the authors are unaware of studies involving detailed characterization and genesis of soils with high activity clays and textural B horizon in the semiarid region of Minas Gerais. Taking into account this region is relatively less dry than the Brazilian semi-arid region, detailed studies involving soil characterization and genesis are justified and incremental to scientific knowledge. Our hypothesis is that the diagnostic B horizon of the studied Luvisols originated from lateral loss of clay from the surface horizons and not from classic argilluviation. Thus, the aim of this study was to detail the genesis of Luvisols of the Semi-arid Depression of the Jequitinhonha Valley (MG), involving morphological, physical, chemical, micromorphological, and mineralogical attributes, and their relationships.

MATERIAL AND METHODS

Study area

The study area is located in northeastern Minas Gerais, in the Middle Jequitinhonha Valley, from 16° S to 16°11' S and 39°57' W to 40°22' W, comprising the municipalities of Salto da Divisa and Jacinto (Figure 1). The climate is semi-arid (Aw) by the Köppen classification (Brasil, 1987; Brasil, 1970), with mean annual rainfall of 800 mm irregularly distributed (ANA, 2016; Brasil, 1987) and mean annual temperature of 23 °C (Araujo, 2000; Brasil, 1987). This region is located in a transition zone (ecotone zone) (Brasil, 1970; Campos et al., 1997), where climate characteristics can influence soil characteristics and genesis.

Native vegetation is represented by Deciduous Seasonal Forest, although quite altered (Araujo, 2000; Brasil, 1987; Brasil, 1970), and a considerable part of the region is currently occupied by pastures. The study area covers two geomorphological units: Marginal Highlands and Central Jequitinhonha Depression. These units are characterized by convex and sharp features and extensive flat areas. Rolling and slightly rolling topography predominates, with altitude ranging from 150 to 300 m (Brasil, 1987), inserted in the Paraguaçu Cycle erosion surface (Brasil, 1970).

The studied soils formed from two parent materials. Profiles P2, P3, and P4 originated from biotite gneiss of the South Paraíba Complex, constituted mainly by feldspars, hornblende, biotite, and quartz (Araújo, 2000; Brasil, 1987). Profile P1 is under the influence of granite of the Medina Complex, with mineralogical constitution similar to the rocks of the South Paraíba Complex (Brasil, 1987), including quartz, feldspars, and biotite.

Morphological analyses

Soil profiles were selected based on morphological features associated with high activity clays. They were collected and described according to Santos et al. (2015), and classified according to Santos et al. (2018), USA Soil Taxonomy (Soil Survey Staff, 2014) and WRB Soil Classification (FAO, 2014). In Soil Taxonomy, they are classified as Alfisols, and in WRB, as Luvisols.

Laboratory analyses

Particle size distribution, water-dispersible clay, particle density, and bulk density were performed in accordance with Donagema et al. (2011).

Fertility analyses comprised the following methods: pH in water and in 1 mol L⁻¹KCl, both in the ratio of 1:2.5 (soil:solution). Available P and K, and exchangeable Na⁺ were extracted by Mehlich-1 solution (1:10 ratio); P was determined by the Vitamin C method (Braga; Defelipo, 1974) and measured by colorimetry; K and Na⁺ were measured by flame emission photometry. Exchangeable Ca²⁺ and Mg²⁺ were extracted with 1.0 mol L⁻¹ KCl (1:10 ratio) and measured by atomic absorption spectrophotometry; and exchangeable acidity (Al³⁺) was extracted by 1 mol L⁻¹ KCl (1:10 ratio) and determined

by titration with NaOH (0.025 mol L⁻¹). Potential acidity $(H^+ + Al^{3+})$ was extracted by 0.5 mol L⁻¹ calcium acetate at pH 7.0 (1:5 ratio) and determined by titration with NaOH (0.025 mol L⁻¹). Soil organic carbon was determined by the Walkley and Black (1934) method, using dichromate $(Cr_{2}O_{7}^{2})$ in acid medium as an oxidant. Remaining P (P-rem) was obtained after shaking 5 cm³ of air-dried fine earth (ADFE) for 1 h with 50 mL of 10 mmol L⁻¹ CaCl, solution containing 60 mg L⁻¹ P (Alvarez et al., 2000). From these results, the following parameters were calculated: sum of bases (SB), effective cation exchange capacity (t), cation exchange capacity at pH 7.0 (T), cation exchange capacity corrected for the clay fraction (CECr) [CECr=(T/%clay)*100)], base saturation (V), and Al saturation (m), according to Vettori (1969), with modifications by Donagema et al. (2011).

The contents of Al_2O_3 , Fe_2O_3 , TiO_2 , and K_2O of the ADFE were determined by atomic absorption

spectrophotometry, and contents of P_2O_5 by molecular absorption spectrophotometry after acid digestion with H_2SO_4 1:1 (volume), according to Vettori (1969), with modifications by Donagema et al. (2011). The contents of crystalline Fe and Al in the clay fraction were determined by atomic absorption spectrophotometry after three successive extractions with sodium dithionite-citratebicarbonate, according to Mehra and Jackson (1960), and their less crystalline contents were determined by a single extraction with acid ammonium oxalate solution, according to McKeague and Day (1966).

Total Cu, Ni, Zn, and Pb were extracted from ADFE by a triacid solution constituted by concentrated $HClO_4$, HNO_3 , and HF (Donagema et al., 2011). Quantification was made by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

For mineralogical characterization by X-ray diffraction, samples of the clay fraction were prepared

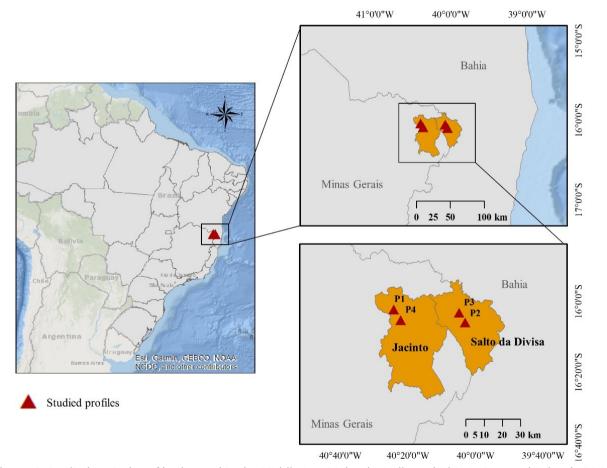


Figure 1: Studied Luvisol profiles located in the Middle Jequitinhonha Valley, whithin Jacinto and Salto da Divisa municipalities, Minas Gerais, Brazil.

onto glass slides and oriented; samples of the silt and sand fractions were mounted on cavity microscope slides (random powder) (Whittig; Allardice, 1986). The following treatments were performed for identification of 2:1 expandable minerals: saturation of the samples with K⁺ and then heating at 350 °C and 550 °C; saturation of the samples with Mg²⁺ and glycerol (Whittig; Allardice, 1986). Samples of the clay fraction were also treated with 5 mol L⁻¹ NaOH (Kämpf; Schwertmann, 1982) and mounted on slides without orientation for identification of Fe oxides. The X'Pert PRO device was used with Co radiation (CoK α) and with Fe filter , in the range of 4 to 50 °20, with a voltage of 40 kV and current of 30 mA.

Undisturbed samples for micromorphological characterization were impregnated with polyester resin, sectioned, polished, and fixed onto glass slides. Micromorphological features were analyzed in an optical microscope and described according to Stoops (2003).

RESULTS AND DISCUSSION

Morphological and physical attributes

The P1 profile presented moderate A horizon with 10YR hue. The color values were 3 or 4, with chromas of 1 or 2 (Table 1). The textural B horizon of P2 profile exhibited reddish color, in spite of being in lower positions in the landscape. The low chroma of the surface horizon that denotes gravish colors results from its organic matter content. With exception of the P2 profile, the textural B horizon of the soils exhibited vellowish brown colors, which are not common in Luvisols of the Northeast region (Oliveira et al., 2004), where reddish colors are found, as were observed by Oliveira et al. (2009) in Paraíba and Pernambuco states. Higher rainfall in the semi-arid region of Minas Gerais in comparison to the semi-arid region of the Northeast are responsible for the yellowish color of the Luvisols of the Middle Jequitinhonha Valley.

The A horizon of all studied soils exhibited subangular blocky structure, while the structure of the B horizon of the soils derived from biotite gneiss (P2, P3, and P4) ranged from strong medium to large angular and subangular blocks. The B horizon of P1 profile, derived from granitic rocks, exhibited prismatic structure composed of angular and subangular blocks with a moderate degree of development. The moist consistency of the A horizon of all studied soils is slightly plastic and somewhat sticky, whereas the consistency of the B horizon is very plastic and very sticky (Table 1). The consistency difference between the subsurface and surface horizons results from the greater clay content in the subsurface horizon and the presence of high activity expandable 2:1 clay minerals identified by X-ray diffractometry (XRD), such as smectite, which was not observed in the A horizon. Wetting and drying cycles and the high activity of clays help to explain the occurrence of crushed roots in the textural B horizon of P4 profile. In addition, the observed roots were fine and restricted to the A horizon of the studied soils.

The transition between the surface and subsurface horizons was clear or abrupt and flat, which is in accordance with the typical textural gradient of Luvisols. The visual contrast between the surface and subsurface horizons is striking, and the textural gradient between the A and B horizons is responsible for this difference. Few and weak clay skins were observed in P1 profile.

The studied soils had the textural B horizon in common. The highest clay content in this horizon was registered in the P1 profile (Table 1).

The silt contents ranged from 58 to 219 g kg⁻¹. In the P2, P3, and P4 profiles, higher silt values were found in the A horizon, decreasing with depth. In P1 profile, however, the highest silt content was observed in the Bt2 horizon. The observed silt contents were relatively low (Table 1). Similar results were found by Sacramento et al. (2019) in soil with Bt horizon and c high activity clays in semi-arid region of Bahia, where probably the striking contraction of this type of clays during the day period contribute to the breakdown of silt particles. Unlike other Luvisols from northeastern Brazil (Oliveira et al., 2009; Fernandes et al., 2010), Nigeria (Ajiboye et al., 2019) and Italy (Costantini et al., 2018), none of the Luvisols in this study have gravel.

The expressionless and unclear clay skins in the upper part of the textural B horizon observed in only 1 out of the 4 studied soil profiles suggests that clay illuviation was not the main formation process of these Luvisols. In Luvisols from Iran, Owliaie, Ghiri and Shakeri (2018) did not identify clay skins in the Bt horizon, and this can be due to the high shrink-swell potential, promoted by high activity clays. The abrupt or clear and flat transition is common in the studied soils and, according to Resende (1983), the flat transition between the A and B horizons favors the idea of formation of the textural gradient by lateral loss of clay from the surface horizons. On the contrary, Sauzet et al. (2016) found clear and smooth or gradual and smooth transitions between the surface horizons and the B horizons, in lluviation studies involving Luvisols with a substantial occurrence of clay skins in a dry and cold region of France.

(cm)		orructure .											
	color		Dry	Moist	Wet			ы В С	g/kg	-		g/kg	%
			P1 – Ab	ruptic P	P1 – Abruptic Palic Chromic Luviso	'isol							
A 0-33 1	10 YR 4/2	Weak M a L bl sub	SIh	fr	SI PI SI Sy	cl fl	527	240	150	83	0.22	38	74
Bt1 33-69 2	2.5 YR 3/6	Mod L bl ang a sub	٨m	fir	Vm Pl Vm Sy	gr fl	239	60	643	58	0.4	249	61
Bt2 69-110 2	2.5 YR 4/8	2.5 YR 4/8 Mod L pris bl ang a sub	Vm h	fir	Vm Pl Vm Sy	gr rl	150	172	459	219	0.09	224	51
Cr 110+							620	148	156	76	0.42	54	65
			P2	Typic Or	P2 – Typic Orthic Haplic Luvisol	o							
A 0-15 1	10 YR 4/2	Mod S bl sub	ے	fr	SI PI SI Sy	ab fl	450	243	221	86	0.19	82	63
Btn 45-70	5 YR 5/3	Str M a L bl ang a sub	۷m h	Vm h Vm fir	Vm Pl Vm Sy	cl fl	345	170	421	64	0.2	332	21
Crn 70-100+	ı	·					737	127	75	61	0.58	26	99
			P3 – So	lodic Or	P3 – Solodic Orthic Chromic Luvisol	/isol							
A 0-20 1	10 YR 3/1	Mod S bl sub	SIh	fr	SI PI SI Sy	ab fl	454	224	206	116	0.2	59	71
Btn 60-80 1	10 YR 5/4	Str L bl ang	Ex h	Vm fir	Vm Pl Vm Sy	cl rl	380	134	379	108	0.3	161	58
Crn 80-100+	ı	ı					687	113	105	96	0.6	26	75
			P4 – So	lodic Or	P4 – Solodic Orthic Chromic Luvisol	/isol							
A 0-18 1	10 YR 3/2	Mod S bl sub	Vm h	Vm h Vm fir	SI PI SI Sy	cl fl	410	212	226	152	0.19	69	69
Btn 18-48 7	7.5YR 4/6	Str M a L bl ang a sub	Vm h	Vm h Vm fir	Vm Pl Vm Sy	gr fl	338	115	400	147	0.3	155	61
Crn 48-75+							611	129	142	119	0.47	46	67

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The water-dispersible clay (WDC) values of these soils were high (Table 1). In all studied soils, there was a tendency of higher degree of flocculation in the surface horizons compared to the subsurface ones, in accordance with the highest soil organic carbon contents. The greater degree of flocculation in the surface horizons (Table 1) is due to the cementing action of the organic carbon and/or to the fact that a large part of clays more susceptible to dispersion had already been transported downwards in the soil profile, and those with greater stability remained. Although the WDC contents were high, they were lower than those observed in similar soils of the Northeast region (Luz; Santos; Mermut, 1992; Oliveira et al., 2009).

The imbalance of the Ca:Mg ratio helps to explain the lower degree of flocculation of the textural B horizon in relation to the A horizon. Because the hydrated ionic radius of Mg is greater than that of Ca (Dontsova; Norton, 2002), on the surface of clays where a greater content of exchangeable Mg⁺ is present, there will be a tendency to absorb more water compared to those clays with predominance of exchangeable Ca²⁺. This reduces the forces that maintain the soil particles aggregated, resulting in an increase in clay expansion and dispersion (Dontsova; Norton, 2002; Qadir et al., 2018).

Soil fertility

All studied soils exhibited pH in water values greater than pH in KCl (Table 2), indicating predominance of negative surface charges. High base saturation (BS) values were found, meaning all soil horizons are eutrophic (V > 50%). The Ca²⁺ and Mg²⁺ contents were generally high, with Ca2+ exhibiting small variation between A and Bt horizons. Mg²⁺ presented higher values in the subsurface horizons. The percentage of magnesium saturation (PMgS) ranged from 20.23% in the A horizon of P2 profile to 69.99% in the Btn horizon of P3 (Table 2). In general, higher contents of Ca²⁺ than Mg²⁺ have been registered in Brazilian Luvisols (Araújo, 2000; Resende, 1983), however, a clear contrary tendency is observed in the studied soils. The high contents of Mg²⁺ are related to the presence of biotite and plagioclases identified by the XRD of the silt and fine sand fractions of these soils (Huang, 1989) (Figures 1C, 1D, 2A, 2B). Mg²⁺, as the predominant cation in the exchange complex, is very important for clay dispersion (Table 3), acting together with Na⁺, since clays saturated with Mg2+ are more chemically stable and do not release electrolytes in the soil solution (Kreit; Shainberg; Herbillon, 1982), being easily dispersed in

water. The sodium saturation of the soils is not as high as the angular and subangular blocky structure and the hardness would indicate.

Various studies have shown that Mg^{2+} acts in clay dispersion and/or in the reduction of hydraulic conductivity (Dontsova; Norton, 2002; Schaefer; Dalrymple, 1996; Oster; Sposito; Smith, 2016; Qadir et al., 2018). Mg^{2+} may have contributed to the formation of the structure observed in the studied soils. In this sense, Schaefer and Dalrymple (1996) observed columnar structure in soils of the Brazilian Amazon region, even with low values of PSS, and they attributed this feature to the high contents of Mg^{2+} .

In general, the percentage of sodium saturation (PSS) was low in A horizons, but substantially increased with depth, being a significant constraint to the growth of most plants. Profiles P1, P3, and P4 exhibited a solodic character, whereas profile P2 has a sodic character, with PSS of 32.89% in the Btn horizon. The sodic character of P2 profile is indicated by nearby presence of "salt water ponds". The highest Na⁺ contents were found in Cr horizons, which agrees with the XRD showing the expressive presence of sodic plagioclases in the silt and sand fractions, which are able to release sodium to the soil solution (Schaefer; Dalrymple, 1996).

The values obtained for soil organic carbon are higher than those found by some authors (Luz; Santos; Mermut, 1992; Corrêa et al., 2003) in Luvisols of the Northeast region of Brazil, and also higher than those found by Sacramento et al. (2019) in other soil classes of semi-arid in Brazil. However, Luvisol profiles studied in Brasil (1987) in the semi-arid region of Minas Gerais registered values of organic carbon similar to those found in this study, very likely due to the less severe climate conditions (seasonal deciduous forest) than in the semi-arid region of the Northeast, dominated by the xeric shrubland ecoregion. Vasu et al. (2018) also found low levels of organic C in soils of semi-arid regions of India and associated the low levels with the degradation of the soils.

Available P contents varied among soils, and all of them exhibited greater content in the A horizon compared to B horizon, a pattern related to the cycling of nutrients and to the organic cycle. P1 was the soil with the highest content in A horizon (9.01 mg kg⁻¹), whereas P3 exhibited the lowest value (0.75 mg kg⁻¹). The phosphorus availability values are low or very low in the studied soils (Ribeiro et al., 1999), in association with the P-fixation by Ca compounds.

Horizon	Depth	đ	Нd	Ca^{2+}	Mg^{2^+}	¥	Na⁺	$A ^{3_+}$	H*+A ³⁺	SB	⊢	t	CECr	BS	E	PSS	PMgS	ю О	٩	P-rem
	cm	H_2O	KCI					- cmol _c /kg	/kg						%			%	mg/kg	kg
								Ρ1	P1 – Abruptic Palic Chromic Luvisol	tic Palic	Chrom	ic Luvi	sol							
Ap	0 - 33	5.30	4.95	0.97	0.89	0.31	0.25	0.10	1.97	2.42	4.40	2.52	29.31	55.11	3.85	5.58 2	20.23	1.51	9.01	37.43
Bt1	33 - 69	5.53	4.49	1.55	11.12	0.20	2.71	0.41	3.17	15.58	18.75	15.99	29.17	83.08	2.58	14.46	59.31	1.46	4.37	29.79
Bt2	69 - 110	5.67	4.40	1.77	16.32	0.13	5.03	0.44	2.48	23.25	25.73	23.69	56.05	90.38	1.84	19.54 6	63.43	1.27	5.63	33.57
Crn	110+	6.59	4.58	1.09	7.35	0.12	2.95	0.29	1.16	11.50	12.66	11.80	81.19	90.83	2.47	23.30 5	58.06		3.08	39.26
								-	P2 – Typic Orthic Haplic Luvisol	c Orthic	Haplic	Luviso	_							
A	0-15	5.73	5.13	1.24	2.26	0.89	0.22	0.04	1.19	4.61	5.80	4.66	26.00	79.56	1.00	3.77 3	38.97	1.55	5.76	52.40
Btn	45-70	5.31	4.28	0.30	6.74	0.01	4.08	0.20	1.28	11.12	12.40 11.32	11.32	29.00	89.66	1.80	32.89 5	54.35	1.39	0.74	47.65
Crn	70-100+	5.88	5.05	0.13	2.34	0.00	1.40	0.04	0.02	3.88	3.90	3.92	52.00	99.38	1.00	36.01 6	60.00	ı	1.39	57.22
								P3	1	Solodic Orthic Chromic Luvisol	Chrom	ic Luvi:	sol							
A	0-20	5.65	5.22	2.61	2.69	0.13	0.10	0.09	1.91	5.52	7.43	5.61	36.00 74.28	74.28	1.50	1.29 3	36.20	1.98	0.75	48.15
Btn	60-80	6.44	5.53	2.59	10.38	0.05	1.34	0.01	0.46	14.37	14.83	14.38	39.00	96.90	0.10	9.03	66.69	1.76	0.29	40.15
Crn	80-100+ 7.40	7.40	6.02	0.75	4.62	0.01	1.14	0.01	0.02	6.51	6.54	6.52	62.00	99.63	0.10	17.43 7	70.64		5.31	58.22
								P4 -	- Solodic Orthic Chromic Luvisol	: Orthic	Chrom	iic Luvi:	sol							
Ap	0-18	5.92	5.26	1.64	2.03	0.53	0.02	0.03	1.72	4.22	5.94	4.25	26.00	71.07	0.70	0.32 3	34.18	1.82	8.74	47.22
Btn	18-48	6.23	4.64	1.00	7.82	0.09	0.92	0.23	1.67	9.82	11.49	10.06	29.00	85.47	2.30	8.02 6	68.06	1.41	0.83	41.31
Crn	48-75+	6.02	4.95	0:30	6.68	0.00	3.95	0.04	0.41	10.93	11.34	10.97	80.00	96.37	0.40	34.86 5	58.91		15.41	29.56

Sulfuric acid digestion, iron and aluminum extracted by dithionite and oxalate in the clay fraction, and total digestion

The contents of Fe_2O_3 extracted by sulfuric acid digestion varied widely among studied soils. The highest value was 10.41 dag kg⁻¹ in the Crn horizon of P4 profile, and the lowest content was registered in the A horizon of P1. The highest Al_2O_3 content was 16.42 dag kg⁻¹ in the Bt1 horizon of P1 profile, and the lowest was 2.27 dag kg⁻¹ in the Crn of P2 (Table 3).

Variation in the Fe₂O₃ contents in the studied soils reflects variations of parent material composition and pedoenvironments. The P1 profile, derived from granitic rock, has higher contents of Fe₂O₃ and Al₂O₃. Higher values of Fe₂O₃ were observed in the subsurface horizons compared to the surface horizons. This is because higher clay contents are found in the subsurface horizons, where the highest proportion of pedogenic Fe oxides are concentrated. The Al₂O₃ contents follow the same distribution pattern of the Fe oxides. The P2 and P3 profiles which are found in the lower third of the landscape, except for the A horizon of P2, exhibit the lowest Fe oxide contents of all horizons and the lowest content of SiO_2 in the surface horizon.

In all soils and horizons, the contents of SiO_2 were greater than Al_2O_3 , indicating low weathering-leaching rates and resulting in Ki values greater than 2.2 (Table 3). Values greater than 2.2 indicate less desilication, due to the low rainfall and moderate drainage that favor maintenance of silica in the system and the formation and maintenance of 2:1 clay minerals, expandable or not, in the clay fraction, as confirmed by XRD (van Breemen; Buurman, 2002; Kämpf; Curi, 2012).

TiO₂ contents ranged from 0.15 in the Cr of P3 profile to 1.29 dag kg⁻¹ in the Bt2 horizon of P1 (Table 3). The parent material is the main soil formation factor that explains the relatively higher contents of Ti oxides in P1, since this profile was developed from granite, and the others were developed from biotite gneiss.

Fe-oxalate/Fe-dithionite ratios ranged from 0.08 to 0.39. The values of Fe oxides having low-crystallinity degree (Fe_o) ranged from 0.24 to 1.23 dag kg⁻¹, exhibiting higher values in the A horizons (Table 3), in association with higher organic carbon content. According to Kämpf

Horizon	Depth	Fe ₂ O _{3 s}	Al_2O_{3s}	SiO _{2 s}	TiO _{2 s}	Ki	Fe _d	Fe _o	Fe _o /Fe _d	Cu _t	Ni _t	Zn _t	Pb _t
	cm		dag	g/kg			dag	g/kg	-			mg/kg	
P1 – Abru	ptic Palic (Chromic	Luvisol										
Ар	0 - 33	1.12	2.79	4.96	0.79	3.03	1.88	0.55	0.29	5.25	21.13	43.25	22.88
Bt1	33 - 69	6.91	16.42	26.65	1.19	2.76	2.11	0.56	0.26	13.00	57.50	71.50	12.50
Bt2	69 - 110	8.03	14.91	28.50	1.29	3.25	2.51	0.39	0.16	19.38	79.63	89.50	8.25
Crn	110+	6.69	6.85	14.93	1.27	3.70	3.15	0.25	0.08	29.75	80.00	114.25	22.88
P2 – Typic	Orthic Ha	aplic Luvi	sol										
А	0-15	1.96	5.05	6.86	0.28	2.31	1.88	0.73	0.39	2.51	3.34	12.76	8.01
Btn	45-70	4.25	10.62	18.16	0.74	2.91	1.95	0.24	0.12	4.58	11.59	22.92	7.96
Crn	70-100+	1.36	2.27	5.68	0.17	4.25	-	-	-	2.04	8.08	21.35	12.97
P3 – Soloc	lic Orthic	Chromic	Luvisol										
А	0-20	2.29	3.99	6.4	0.38	2.72	3.94	1.23	0.31	1.91	6.62	21.25	13.89
Btn	60-80	4.07	8.81	16.58	0.53	3.2	2.73	0.28	0.10	7.37	15.84	41.92	16.37
Crn	80-100	2.14	2.96	5.64	0.15	3.24	-	-	-	9.56	8.50	19.27	43.89
P4 – Soloc	lic Orthic	Chromic	Luvisol										
Ар	0-18	2.44	4.64	7.41	0.39	2.71	2.71	0.97	0.36	5.00	7.46	33.93	18.17
Btn	18-48	5.47	10.22	17.93	0.86	2.98	2.29	0.41	0.18	4.09	15.72	63.08	13.63
Crn	48-75+	10.41	10.87	19.09	1.45	2.98	-	-	-	20.4	35.1	128.34	9.12

Table 3: Fe, Al, Si, and Ti oxides extracted by sulfuric acid digestion, Fe extracted by dithionite-citrate-bicarbonate (Fe_d) and ammonium oxalate (Fe_d), and trace elements extracted by total digestion.

* s – sulfuric acid digestion; ki index - SiO₂/ Al₂O₃ molecular ratio; t – total digestion.

and Schwertmann (1982), the functional groups of organic matter have affinity with the surface sites containing iron, reducing the crystallization of the Fe oxides by complexation. Similar tendency and interpretation was found by Silva et al. (2019) in soils with Bt horizon in South region of Brazil.

The values of the Fe_o/Fe_d ratio (> 0.05) indicate a substantial proportion of poorly crystallized oxides in the clay fraction of all profiles, as indicated by Inda Junior and Kämpf (2003) and this characteristic is common in soils of semi-arid regions (Corrêa et al., 2003). The Fe_o/Fe_d ratio decreased with depth in all profiles, which denotes greater crystallinity degree of the Fe oxides in the subsurface horizons, especially due to the lower contents of organic carbon.

The trace elements Cu, Ni, and Zn accumulated either in the Cr horizon or in the Bt horizon, with predominance in deeper horizons (Table 3). The predominance of these elements in the horizons indicates a strong relationship to the parent material. Significant correlations at 1% significance were observed between the contents of Fe₂O₃ from sulfuric acid digestion and Cu (0.87***), Ni (0.93***), and Zn (0.87***) of the studied soils. This is explained by the geochemical affinity between iron and these trace elements that can isomorphically replace Fe in the structure of the oxides (Kämpf; Curi, 2000). Thus, Fe oxides are considered reserve sources of these trace elements in soils (Ferreira et al., 1994; Resende et al., 2019).

According to the Resolution 420/2009 (CONAMA, 2009), the contents of trace elements of most studied soils are below the prevention values. However, P1 and P4 profiles exhibit horizons with high content of Ni (80 and 35 mg kg⁻¹ of soil, respectively), values which are above the prevention value (value above which the environment is considered contaminated) (30 mg kg⁻¹ of soil), suggesting additional environmental monitoring.

Mineralogy of the clay fraction

In the clay fraction of the A and Bt horizons of the studied soils, the peaks at 1.42, 1.01, and 0.722 nm indicate the presence of smectite, illite, and kaolinite, respectively. The peaks at 0.418 and 0.269 nm correspond to goethite and hematite, respectively. The peak at 0.333 nm corresponding to quartz was also identified (Figures 2 a, b). In the iron-free clay fraction, smectite was identified in the Bt horizon of P1 and P3 profiles (Figure 2b). Zhang et al. (2016) also identified smectite, ilite, and kaolinite in Alfisols originated from gneiss and granite under different climatic conditions in eastern China. In a semi-arid region of Morocco, Omdi, Daoudi and Fagel (2018) identified illite, associated with kaolinite and smectite in the clay fraction of various soils originated from calcareous rocks.

The presence of quartz in the soil clay fraction may be related to its breakdown to clay size by physical weathering. Eolian transport of particles may also explain the presence of this mineral in the clay fraction, considering that the greatest content of this mineral is found in the surface horizons of the studied soils. Other authors also found quartz in the clay fraction of poorly developed soils (Allen; Hajek, 1989; Fernandes et al., 2010), which may be related to this mineral's smaller resistance to weathering in the soil clay fraction, due to its higher specific surface area.

The identification of smectite in the XRD was based on the expansion of the peak at 1.5 nm in the treatment with Mg^{2+} to 1.8 nm with Mg + Gl (saturation with magnesium and glycerol), and then to the collapse of this peak to 1.3 nm with K-25 °C and to 1.0 nm with K-350 °C. Greater peaks of smectites were found in the subsurface horizons of P3 profile. According to Luz, Santos and Mermut, (1992), this tendency may be related to the accentuated smectitekaolinite alteration in the surface horizons or, according to Azevedo and Vidal-Torrado (2009), the preferential translocation of smectite compared to kaolinite within the soil profile can occur. This is because expandable clay minerals with high superficial charge and smaller particle size have greater mobility than kaolinites (van Breeman; Buurman, 2002; Omdi; Daoudi; Fagel 2018).

The A horizon of the soil profiles exhibited similarities in clay fraction mineralogy, showing illite (1.01 and 0.281 nm), kaolinite (0.446, 0.256, and 0.238 nm), and goethite (0.418 nm) (Figure 2A). In the P2 and P4 profiles, expandable 2:1 clay minerals were not found in the X-ray diffractograms, although the corrected CEC for the clay fraction (CECr) was greater than 27 cmol_c kg⁻¹ of clay in both soils (Table 2). There are two possibilities which may have limited their identification: the small content of expandable 2:1 clay minerals and/or their low crystallinity degree (Resende et al., 2011; Kämpf; Marques; Curi, 2012). In the studied soils, kaolinite and illite were the main clay minerals found.

Goethite is the Fe oxide with the greatest expression in these soils, explained by the slow Fe release due to the semi-arid climate, resulting in low Fe³⁺ content in the soil solution (Resende et al., 2011). Even in the reddish soil profiles (P2 and P4), goethite was the main identified Fe oxide, because this oxide has high thermodynamic stability (Cornell; Schwertmann, 1996). Moreover, water restriction conditions impose low Fe release rates from the structure of primary minerals, especially biotite in this case, hindering hematite formation.

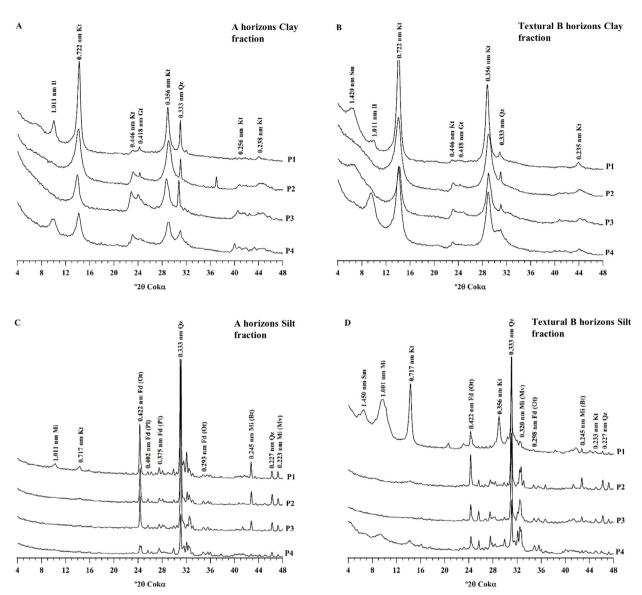


Figure 2: X-ray diffractograms of the Luvisols. A: Clay fraction of A horizons. B. Clay fraction of textural B horizons. C. Silt fraction of A horizons. D. Silt fraction of textural B horizons. Sm - smectite, Kt – kaolinite, II – illite, Hb – hornblende, Mi - mica, Bt - biotite, Mv - muscovite, Fd - feldspar, Ot - orthoclase, PI - plagioclase, Qz – quartz.

Mineralogy of the sand and silt fractions

The fine sand fraction of the A and B horizons presented the following primary minerals in common: quartz (identified by the peaks at 0.333 and 0.227 nm), feldspars (0.422, 0.388, 0.368, 0.347, and 0.293 nm) and micas (0.320, 0.269, 0.245, and 0.223 nm). The mineralogy of the silt fraction, in general, is similar to that of the fine sand fraction, basically constituted of feldspars, micas, and quartz, as well as smectite and kaolinite (Figures 2C,

2D, 3A, 3B). These two clay minerals have better defined reflections in the subsurface horizons, in line with smaller organic carbon values.

These results show that studied soils exhibit a considerable reserve of nutrients, due to the presence of plagioclases, orthoclase, and biotite in the silt and fine sand fractions, and also due to the low degree of weathering-leaching imposed by the semi-arid climate. These primary minerals are mainly responsible for the high exchangeable

plagioclases, and calcite, especially of the silt fraction, in

the increase in the contents of Ca²⁺, Mg²⁺, and K⁺ in the

soil. Corrêa et al. (2003) also associated the high contents

of Ca²⁺, Mg²⁺, and K⁺ in soils of the semi-arid Brazilian

Northeast to the presence of feldspars (plagioclases and

in the clay fraction is due to the transformation process

occurred in the easily weatherable primary minerals. The

expressive peaks of mica and feldspars in the sand fraction

of P1 indicate the origin of smectite and illite from the

weathering of those minerals. In South China, Ndzana et

al. (2019) verified the disappearance of feldspar peaks in

finer soil particles in and attributed the origin of the illite

to the weathering of the feldspars. The weathering of

micas was also pointed as the origin of illite in soils in flat,

concave and convex landscapes in the semi-arid region of

plagioclase in the silt and fine sand fractions of all analyzed

soil horizons, minerals which are main components of the

respective parent rocks, indicates the in situ formation of

these soils. The low weathering-leaching conditions of

the soils in the study area favor biotite persistence in the

The presence of biotite, muscovite, orthoclase, and

northeastern Brazil (Oliveira et al., 2018).

The identification of smectite in the silt fraction of Bt horizon of P1 suggests that the genesis of this mineral

microcline) in the sand and silt fractions.

Even with different parent materials, the Luvisols derived from biotite-gneiss and granite exhibited similar coarse fractions mineralogy, compatible with the low pedogenic development of these soils, conditioned by the semi-arid climate.

Soil micromorphology

In P1 profile, in general, there is predominance of fissured microstructure (Stoops, 2003), with unconnected vughs and planar pores which are poorly to moderately accommodated (Figure 4A). Also, there is less biotite and therefore voids are mainly marked by fractures and twin planes. The groundmass is diversified, reflecting the mineralogical diversity in the crude material and the formation of clay minerals and oxidic clays in the micromass.

Regarding pedological features, clay coatings were observed (Figures 4B, C). These coatings are of two types, considering their color and composition: i) reddish coatings (golden in crossed nicols), suggesting a more ferruginous composition, argilloferran type (Figure 4C); and ii) light colored coatings (only argillans), with silicate clay composition, marked by silvery colors when observed in crossed nicols (Figure 4B).

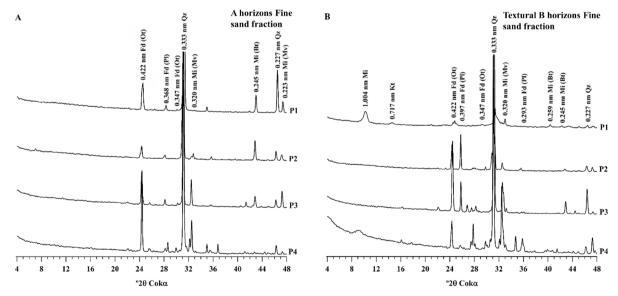


Figure 3: X-ray diffractograms of the fine sand fraction of the Luvisols. A: Sand fraction of the A horizons. B. Sand fraction of the textural B horizons. Kt – kaolinite, II – illite, Hb – hornblende, Mi - mica, Bt - biotite, Mv - muscovite, Fp - feldspar, Ot - orthoclase, PI - plagioclase, Qz – quartz.

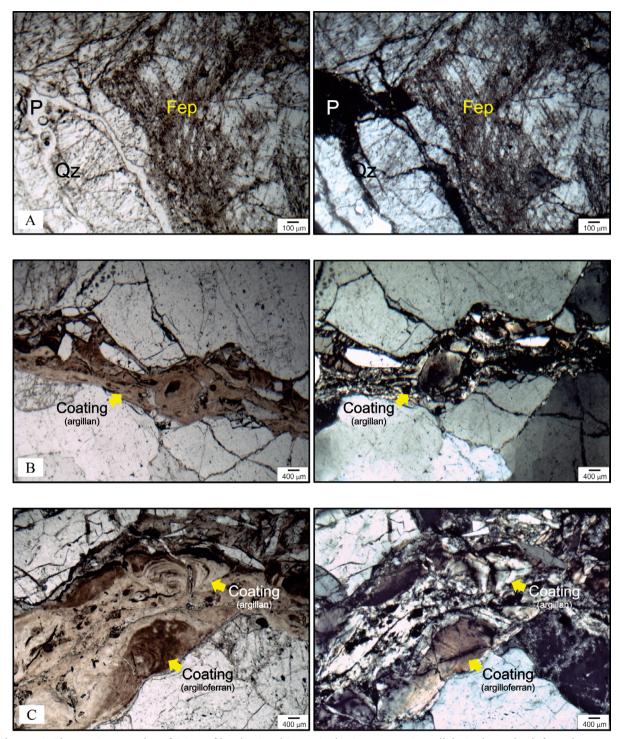


Figure 4: Photomicrographs of P1 profile obtained in optical microscope (parallel nicols to the left and crossed ones to the right). A – altered alkaline feldspar crystals (kaolinized) along fractures and cleavage planes; B and C – saprolyte horizons at the isalteritic level (CR horizons) showing textural features associated with accumulation of clay within voids and/or grain surfaces, separated in crossed nicols by color in argillans (B) and argilloferrans coatings (C). Qz - quartz; Fep - feldspar; P – void.

The coatings of P1 profile mainly fill the planar pores and are arranged parallel to the surfaces of these pores (porostriated b-fabric) or oriented according to the surfaces of mineral grains (granostriated b-fabric). They differ from the micromass by the shades, interference colors, and clarity, so they should not be confused with alteromorphs of biotite (Kühn et al., 2018). As pedofeatures, the presence of coatings in the textural B horizon is intensified in two types (argillans and argilloferrans). In some parts of the thin sections, loose continuous infillings are observed, indicating bioturbation (Figures 5B, C) (Kühn et al., 2018).

The textural B horizons are characterized by the presence of angular blocky microstructures, moderately accommodated, not very developed, and with interaggregated planar voids (Figures 5A, B, C, D, E, F). Within the blocks, the groundmass is formed by coarse mineral grains, with predominance of quartz, alkaline feldspar, biotite, and opaque minerals, in this order. Quartz occurs in an angular shape, in sizes that range from fine to medium sand, with some isolated crystals in the size of coarse sand (Figure 5D).

The groundmass in the textural B horizon of P4 profile presents a porphyric relative distribution pattern between coarse and fine constituents, both within the blocks and in the massive domain (Figure 5E).

In the Bt horizon of P4 profile, the coarse constituents are represented by angular quartz crystals, in size of medium to fine sand, poorly selected, and quite fractured. Equally common are biotite pallets, with diverse degrees of alteration, as well as plagioclase crystals.

The micromass exhibits a reddish-yellow color in the textural B horizons of P4 profile, where there is a notable color difference in the interior part and at the edge of the aggregates. Regarding birefringence fabrics, these soil horizons show predominance of parallel striated and granostriated b-fabrics.

The microstructure of the textural B horizon of P4 profile consists mainly of fissured domains, without developed pedality, and by angular and subangular blocks, partially accommodated or not accommodated (Figures 5E, F).

Considering the constituents and the aforementioned micropedological organizations of the P4 profile, an important point should be highlighted regarding their significance to the genesis of the studied soils. This point is related to the mineralogy of the coarse constituents, that even in the more relatively developed soil horizons, includes many easily weatherable primary minerals, reiterating the low degree of alteration of these soils. Furthermore, a large number of biotite alteromorphs was observed, which are more frequent and with a lower degree of alteration at the bottom of the textural B horizon. Plagioclase crystals, partially altered to kaolinite, were also identified.

The main pedological features in the studied soil horizons were textural features, coatings, and nodules. In relation to textural features, very few typical growing coatings were observed; stress and hypocoatings were more common. The stress coatings occur in textural B horizons associated with vughs and grain surfaces, suggesting reorganization of constituents by contraction and expansion movements of the 2:1 clay minerals. They have b-fabric orientated nearly perpendicular to the surface of contact, which indicates that they were formed by reorganization of the micromass and not by clay deposition. The hypocoatings were observed as impregnations of the groundmass within the aggregates and seem to be associated with zoning of defined chemical constituents, in this case, edge ferrugination zones.

Several features similar to clay coatings were observed in soil depth, indicated by the strong shine and increased orientation of the constituents, being not interpreted as textural pedofeatures (illuviation processes). They are oriented clays associated with biotite alteromorphs, occurring when pallets were in degrees 4 and 5 of alteration and clay films were associated with reorganization of the micromass, already mentioned as stress coatings. The difficulty in distinguishing such features and the precautions to correctly interpret them were indicated by Kühn et al. (2018).

In most of the textural B horizons, the pores are open and do not present clay coating. Stress coatings are present, which are associated with reorganization mechanisms of fine constituents during wetting and drying cycles. These observations corroborate field macromorphological aspects concerning the lack of illuviation coatings (clay skins) in P2, P3, and P4 profiles. The strong orientation of the clay in diverse domains, both at the edges of the grains and inside the aggregates themselves, is related to orientation preservation of the primary phyllosilicates and not to deposition of the translocated clay. Several studies have corroborated these findings (Campos et al., 1997; Phillips, 2004; Oliveira et al., 2008). Therefore, the lateral loss of clay from the surface horizons is highlighted, as occurs in most soils (cohesive Yellow Argisols) of the Brazilian Coastal Plains (Curi; Ker, 2004; Carvalho Filho; Curi; Fonseca, 2013).

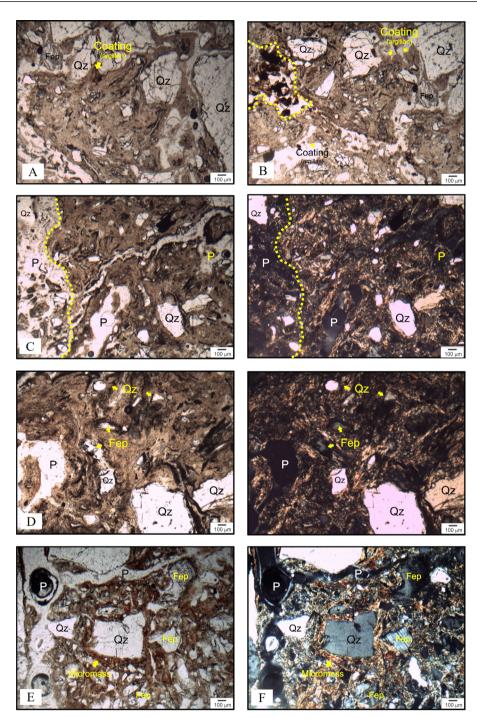


Figure 5: Photomicrographs obtained in optical microscope (parallel nicols to the left and crossed ones to the right, except for images A and B, where only images in parallel nicols were presented) of the textural B horizons of P1 profile, showing: A, B, C, and D: weakly developed angular blocks with micromass in a brownish red tone, derived from alteration of granite. There are more site-specific argilloferrans coatings, generally located on the surfaces of quartz grains. Bioturbated zones are highlighted, indicated in dotted yellow lines. Qz = quartz; Bt = biotite; PI = plagioclase; Fp = alkaline feldspar; P = pore. Objectives with 4X increase (A, B, C, D); E and F: photomicrographs of the textural B horizon of P2. Qz = quartz; Bt = biotite; PI = plagioclase; P = void.

Integrated interpretation of the main data

The main attributes included in the various field and laboratory analyses tended to a consistent convergence in terms of soil genesis and related pedological features. Between these findings, the most striking one refers to the elutriation process (lateral remotion of clay particles from the superficial horizons without substantial clay translocation, which is the classic process of soil formation of argillic horizons). The other important achievement was the very adequate match between macro- and micromorphology approaches, placing emphasis on the need of such complementary analyses in detailed soil genesis studies.

Finally, this study registered remarkable lower values of cation exchange capacity of Luvisols in semiarid Brazilian conditions.

CONCLUSIONS

The similarity of the coarse fractions mineralogy of the Luvisols derived from different parent materials points out the climate as the main factor of soil formation. The expressionless and unclear clay skins observed during the field work in the top of B horizon in only one out of the four soil profiles studied, and the lack of illuviation coatings in laboratory micromorphological analysis, indicate that clay translocation was not the main process in the formation of these Luvisols, where the lateral loss of clay from the superficial horizons stood out.

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