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**Division - Soil in Space and Time** | Commission - Soil Genesis and Morphology

# Genesis and Classification of Soils Containing Carbonates in a Toposequence of the Bambuí Group

Deyvid Diego Carvalho Maranhão<sup>(1)</sup>, Marcos Gervasio Pereira<sup>(1)\*</sup>, Leonardo Santos Collier<sup>(2)</sup>, Lúcia Helena Cunha dos Anjos<sup>(1)</sup>, Antonio Carlos Azevedo<sup>(3)</sup> and Rafael de Souza Cavassani<sup>(1)</sup>

- (1) Universidade Federal Rural do Rio de Janeiro, Departamento de Solos, Seropédica, Rio de Janeiro, Brasil.
- (2) Universidade Federal de Goiás, Escola de Agronomia, Escola de Agronomia e Engenharia de Alimentos, *Campus* Samambaia, Goiânia, Goiás, Brasil.
- (3) Universidade de São Paulo, Escola Superior de Agricultura "Luiz de Queiroz", Departamento de Ciência do Solo, Piracicaba, São Paulo, Brasil.

ABSTRACT: The Bambuí Group, formed from siliciclastic sediments deposited on an extensive epicontinental platform at the end of the Neoproterozoic era, is characterized by limestones with fine to very fine texture. Limestone-derived soils in the southeast of Tocantins state, Brazil, are less notorious than similar soils in other regions of Brazil and their characterization could contribute to the Brazilian System for Soil Classification (SiBCS). Given that little is known of these soils, despitetheir agricultural potential, the objective of this study was to characterize their properties and the processes leading to soil of genesis, and also contribute to developing the Brazilian System of Soil Classification (SiBCS). Soils profiles were located on the summit (P1), shoulder (P2), backslope (P3), and footslope (P4) of a toposequence in the municipality of Lavandeira, Tocantins. Morphological, physical, chemical, and mineralogical properties of the profiles were determined. The soils were classified as: P1 - Chernossolo Rêndzico Lítico típico (Lithic Haplustolls); P2 - Cambissolo Háplico Ta Eutrófico léptico hipocarbonático (Lithic Haplustolls); P3 - Cambissolo Háplico Carbonático léptico (Lithic Haplustepts); and P4 - Luvissolo Háplico Órtico típico (Typic Rhodustalfs). All the profiles showed high contents of silt, calcium, and magnesium, which resulted in high pH and low exchangeable aluminum content. Base saturation and calcium carbonate equivalent contents were also high, and the horizons showed dark colors due to high organic matter content, which contained humin as the dominant fraction. Mineralogical analysis of the clay fraction indicated predominance of hydroxy-interlayered vermiculite, followed by illite, kaolinite, and quartz, whereas the sand fraction exhibited reflections characteristic of the quartz mineral. Given P4 contents of calcium carbonate equivalent above 50 g kg<sup>-1</sup> and the relevance of this feature for agriculture, we propose the inclusion of hypocarbonate as a criterion for classification of *Luvissolos Háplicos Órticos* at the subgroup level.

**Keywords:** karst environments, SiBCS, dry forest, carbonate character.

\* Corresponding author: E-mail: gervasio@ufrrj.br

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#### INTRODUCTION

The Bambuí Group is a geological formation that covers 300 000 km² of the São Francisco Craton (Dardenne, 1978), located in the eastern portion of the Brasília fold belt (Dardenne, 2000). On a geological time scale, pelagic carbonate sediments, followed by siliciclastic sediments (Dardenne, 1978), were deposited in the area during inversion tectonics of the basin, ca. 790-600 Ma (Santos et al., 2000). The Bambuí Group is characterized by argillite, limestone, siltstone and fossilized stromatolites (Santos et al., 2000). The limestones are stratified and exhibit very fine to fine particles, are grayish in color, and contain calcite surrounded by hematite inclusions and diffuse carbonate materials (Embrapa, 1983). Soils formed from limestone parent material cover a significant portion of the world's agricultural lands (Chen and Barak, 1982).

In Brazil, the agricultural potential of most calcareous soils is related to high Ca and Mg contents, low Al activity, and high base saturation and pH. Soil classes formed from Bambuí Group limestones in Tocantins are *Gleissolos*, *Nitossolos* and *Cambissolos*. They exhibit slightly acidic pH, high Ca and Mg contents, and base saturation above 50 % (Embrapa, 1983). In an area with similar geology in the state of Goiás, *Cambissolos*, *Vertissolos*, and *Argissolos* (similar to Inceptisols, Vertisols, and Ultisols/Alfisols, respectively) with high base saturation and medium to clayey texture were observed (Brasil, 1982).

The lower plateaus in Northeast Brazil exhibit *Cambissolos and Vertissolos* derived from Jandaíra Group limestones, with pH above 7 and base saturation above 90 % (Lemos et al., 1997), as well as *Organossolos* (Histosols) (Silva et al., 2014). Also in Northeast Brazil, *Vertissolos* with high-activity clay and high contents of Ca and Mg, originating from calcareous sediments, are found in the Fernando de Noronha Archipelago, Pernambuco (Marques et al., 2014). Limestone-derived soils with high base saturation and pH occur in the north of the state of Minas Gerais (MG), in the Jaíba Project area (Oliveira et al., 2000), particularly *Latossolos* (Oxisols), *Cambissolos*, and *Argissolos*. In contrast, *Latossolos* formed from meta-limestone associated with gabbro, with a very clayey texture, low Ca and Mg contents, and low base saturation, are found in the south of Minas Gerais (Araújo et al., 2014). The occurrence of *Latossolos Vermelhos*, with high base saturation, and *Chernossolos Ebânicos* (Mollisols), with pH near 6.0 and low Al activity, was described in the Serra do Paranoá, Goiás (Lynch, 2009). Calcareous soils in the Serra da Bodoquena, Mato Grosso do Sul (MS), are represented by *Organossolos* (Histosols), *Chernossolos* (Mollisols), and *Gleissolos Melânicos* (Aquents) with high base saturation and Ca and Mg contents (Pereira et al., 2013).

Limestone-derived soils in the southeast of Tocantins state, Brazil, are less notorious than similar soils in other regions of Brazil and their characterization could contribute to the Brazilian System for Soil Classification (SiBCS), as well as contributing for better evaluation of agricultural potential.

The objective of this study was to characterize the morphological, physical, chemical, and mineralogical properties of soils formed from Bambuí Group materials, in the municipality of Lavandeira, Tocantins; identify the processes underlying their pedogenesis; and contribute to developing the SiBCS.

# **MATERIALS AND METHODS**

#### **Study Area**

The study area is located in the municipality of Lavandeira, in the southwest of Tocantins, within the Bambuí Group geological formation. The climate according to the Köppen classification system is C2wA'a' (dry sub humid with moderate water deficit) and annual rainfall is 1,500 mm (Köppen, 1948). Local vegetation is classified as "mata seca" (dry forest), a deciduous tropical forest (Ribeiro and Walter, 2008), which is typical of limestone areas (Silva and Scariot, 2003). The topography is slightly rolling to rolling (Embrapa, 1983), with apparent karstic features and limestone outcroppings with signs of carbonate dissolution.



The toposequence was selected in an area with slightly rolling topography. The soil profiles were observed and sampled in pits opened across the slope, on the summit (P1), shoulder (P2), backslope (P3), and (P4) footslope. The profiles studied (P1 to P4; Table 1) were described according to the Brazilian Field Handbook for Soil Sampling and Description (Santos et al., 2013a).

## Laboratory soil analysis

The samples were processed into air-dried fine earth (ADFE) to analyze physical and chemical properties. Particle size was determined by the pipette method, using 0.1 mol  $L^{-1}$  NaPO $_3$  and water, and soil bulk density (BD) was assessed by the Kopecky ring method. The Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup> were extracted with 1 mol  $L^{-1}$  KCl solution, and H+Al was extracted using a 0.5 mol  $L^{-1}$  solution of calcium acetate at a pH of 7. Soil P, Na<sup>+</sup>, and K<sup>+</sup> were determined using the extraction solution of 0.0125 mol  $L^{-1}$  H<sub>2</sub>SO $_4$  + 0.05 mol  $L^{-1}$  HCl; Ca<sup>2+</sup> and Mg<sup>2+</sup> contents were determined by titration with 0.0125 mol  $L^{-1}$  EDTA; Na and K by flame photometry; and Al<sup>3+</sup> and H+Al by titration with 0.025 mol  $L^{-1}$  NaOH. Soil pH was determined in water and KCl (1:2.5 weight), in a direct reading potentiometer. The protocols were based on Claessen (1997). P was extracted using an alkaline solution of 0.5 mol  $L^{-1}$  sodium bicarbonate (Olsen et al., 1954) and measured by colorimetric procedures. The results obtained were used to calculate sum of bases (SB), cation exchange capacity (CEC), base saturation (V), and Al saturation (m).

Sulfuric acid digestion was applied to extract Fe, Al, Ti, and silica (Claessen, 1997), which were expressed as oxides ( $Fe_2O_3$ ,  $Al_2O_3$ ,  $TiO_2$ , and  $SiO_2$ ). Dithionite citrate bicarbonate solution was used to extract Fe from oxides with high and low crystallinity (Fed) (Mehra and Jackson, 1960), and acid ammonium oxalate solution to extract Fe from poorly crystalline compounds (Feo) (Claessen, 1997).

The  $CaCO_3$  contents were determined by sample digestion in 0.5 mol  $L^{-1}$  HCl in excess followed by titration of excess acid with standard NaOH solution (Claessen, 1997). The method was modified by applying a temperature of 250 °C for 10 min.  $CaCO_3$  was calculated by the expression:

$$m_{CaCO_3}(g) = n_{CaCO_3}(mmol) \times M.M._{CaCO_3}(g mmol^{-1})$$

where

$$M_{NaOH} \times V_3 = n_{NaOH} = 1 n_{HCl in excess}$$

$$n_{HCl added} = M_{HCl added} \times V_{HCl aliquot}$$

$$n_{HCl \text{ added}} - n_{HCl \text{ in excess}} = n_{HCl \text{ reacting}}$$

$$n_{CaCO_3} = n_{CaO} = \frac{1}{2} n_{HCl reacting with limestone}$$

where M.M. is molar mass; V is volume; and n is normality.

The organic carbon (OC) contents and chemical fractioning of organic matter were measured according to Yeomans and Bremner (1988) and Benites et al. (2003).

Clay fraction minerals were identified by X-ray diffraction (XRD) from oriented slides mounted with total clay suspension (<2.0  $\mu$ m), without eliminating Fe oxides (Claessen, 1997). Analyses were performed using a Rigaku D-Max  $\Pi$ A diffractometer, with K $\alpha$  radiation ( $\lambda$  = 0.015405 nm) emitted from a copper tube (20 to 25 kv and 10 mA), with a scanning range of 1°20 min<sup>-1</sup> (Claessen, 1997). The sample was pretreated by heating it to 550 °C and saturating it with ethylene glycol and dimethyl sulfoxide, followed by X-ray irradiation. Samples of the sand fraction were ground in a ball mill, and the resulting crystalline powder was mounted on non-oriented slides. The slides were analyzed by XRD, using a Bruker AXS D8 Advance X ray diffractometer that emitted CuK $\alpha$  radiation ( $\lambda$  = 0.015405 nm) from a copper tube (40 kV and 40 mA), with a scanning range of 1°20 min<sup>-1</sup> (0.04°/s). To identify the minerals in the samples, the diffractograms were analyzed using the 2004.04.67 PROX powder software (available at http://www.xpowder.com).



Table 1. Overall description of soil profiles (Prof) in the toposequence in Lavandeira, TO, Brazil

Prof	Location	Slope position Elevation		Land cover	Stoniness	Rockiness
			m			
P1	12°41′49.0″S 46°22′54.0″W	Summit	548	Deciduous Tropical Forest	Very stony	Extremely rocky
P2	12°41′50.0″S 46°22′54.0″W	Shoulder	547	Deciduous Tropical Forest	Stony	Rocky
Р3	12°41′50.0″S 46°22′55.0″W	Backslope	547	Deciduous Tropical Forest	Slightly stony	Slightly rocky
P4	12°41′50.0″S 46°22′57.0″W	Footslope	545	Pasture grass	Nonstony	Nonrocky

The soil profiles were classified according to the Brazilian System of Soil Classification (SiBCS) (Santos et al., 2013a) and Soil Taxonomy (Soil Survey Staff, 2014).

## **RESULTS AND DISCUSSION**

#### **Morphological Properties**

Surface horizons exhibited dark colors due to high organic matter content formed by deposition of plant residues and their interaction with the soil mineral fraction. Subsurface horizons exhibited hues from 2.5 to 7.5YR, ranging from red to orange. Profile P4 showed a hue of 2.5YR in the subsurface horizons, which is typical of soils formed under good drainage conditions and/or from parent materials with high mafic mineral content (Silva and Vidal Torrado, 1999). Reddish hues are associated with the presence of hematite, an iron oxide common to calcareous soils (Boero et al., 1992). Profiles P1, P2, and P3 ranged from reddish-yellow to yellow (5 to 10YR), indicating predominance of goethite over hematite. These colors are developed by a pedogenic process called *brunificação* (brown soil coloring) (Arnold, 1983; Kämpf and Curi, 2012), which is favored by organic matter build-up (Almeida et al., 2000), lower Fe content in the parent material, and poor drainage because of lithic or paralithic contact.

Surface horizons showed predominance of granular structure, and aggregation was improved by high organic matter content. A similar structure, with a moderate to strong degree of development, granular or angular shape, and subangular blocks, was observed in the subsurface horizons of all profiles. The most highly developed structure was associated with the presence of high activity clay (CEC  $\geq 27~\text{cmol}_\text{c}~\text{kg}^{-1}$  of clay) and the aggregating effect of the cations calcium and magnesium. In the pedogenesis of calcareous soils of the Serra da Bodoquena, Mato Grosso do Sul, Silva (2013) attributed the aggregation events and the blocky structure formation to intense wetting/drying cycles and high clay content (>280 g kg $^{-1}$ ). The waxy aspect covering the surface of aggregates in P4 (Table 2) is identified in the field as clay skins (Santos et al., 2013b). The Bt $_1$ k $_5$  and Bt $_2$ k $_6$  horizons had common and moderate clay skins, resulting from the multiple pedogenic processes of clay translocation (Kämpf and Curi, 2012).

The textural classes ranged from loamy to very clayey, and the contents of silt and clay fractions stood out. This is related to the parent material, which is mainly limestone with argillite and laminated siltstone (Embrapa, 1983), in addition to the influence of sediments.



## Physical and chemical properties

With respect to soil granulometry, observed by texture in the field, the content of silt is higher than the content of the other fractions, ranging from 310 to 530 g kg $^{-1}$  (Table 3). High silt contents were found in other soil profiles in the study area (Embrapa, 1983). The presence of laminated siltstone associated with limestone from the Bambuí Group (Dardanne, 1978; Santos et al., 2000) explains the predominance of silt in the profiles. Clay contents ranged from 290 to 520 g kg $^{-1}$  (Table 3), which usually increased in the B horizons and decreased towards the Ck $_5$  horizon. In P4, clay values increased from 290 g kg $^{-1}$  in the Apk $_1$  horizon to 470 g kg $^{-1}$  in Bt $_2$ k $_6$ . In general, the sum of clay and silt contents accounted for more than 70 % of the fine earth (smaller than 2.0 mm) fraction.

The wide variation in the sand fraction in each profile may be associated with the origin of the parent material, from sediment deposition. The variation from a coarse to fine sand ratio in horizons  $Ck_5$  and  $Bt_2K_6$  of P2 and P4 could indicate lithological discontinuity,

Table 2. Morphological properties of soil profiles in the toposequence in Lavandeira, TO, Brazil

Harizan	Donth	Col	or	Structure <sup>(1)</sup>	Clay skins <sup>(2)</sup>	Texture
Horizon	Depth	Wet	Dry	Structure	Clay Skins	class <sup>(3)</sup>
	m					
		Chernoss	solo Rêndzico l	Lítico típico (Lithic Haplustolls) - P1		
$A\overline{k}$	0.00-0.08	7.5YR 3/1	7.5 YR 4/3	st, sm, gr.		cl-lo
ACrk	0.08-0.25	7.5YR 2.5/3	7.5 YR 4/3	st, sm, gr /mo, sm, sb		cl-lo
R	$0.25 - 0.40^{+}$	-	-	-	-	
	Cami	bissolo Háplico	Ta Eutrófico le	<i>éptico hipocarbonático</i> (Lithic Haplusi	tolls) - P2	
$Ak_1$	0.00-0.05	7.5YR 3/2	7.5 YR 4/3	mo, me, ab, gr		cl-lo
$ABk_2$	0.05-0.10	7.5YR 2.5/2	7.5 YR 4/3	mo, me/ sm, ab, gr		cl-lo
BAk <sub>3</sub>	0.10-0.18	7.5YR 3/3		mo, sm, ab		cl-lo
Bik <sub>4</sub>	0.18-0.31	7.5YR 3/3		mo, sm, ab		si-cl-lo
Ck <sub>5</sub>	0.31-0.46	10YR 2/2		wk, sm, gr, sg		cl
		Cambissolo	Háplico Carbo	<i>nático léptico</i> (Lithic Haplustepts) - P	3	
$Ak_1$	0.00-0.05	5YR 3/2	5 YR 4/3	st, me / sm, sb		cl-lo
$AB\bar{k}$	0.05-0.10	5YR 4/4	5 YR 3/2	st, lg /me, ab		cl
Bik <sub>2</sub>	0.10-0.33	5YR 3/4		mo, me, pr, ab		cl-lo
R	0.33-0.50+	-		-		-
		Luvisso	olo Háplico Órt	ico típico (Typic Rhodustalfs) - P4		
$Apk_1$	0.00-0.08	5YR 4/4	5Y	'R 3/3 mo, sm/vsm, gr		cl-lo
$ABk_2$	0.08-0.13	5YR 3/2	5Y	'R 4/4 mo, me/ sm, ab, s	sb	cl-lo
$BA_1k_3$	0.13-0.18	2.5YR 3/2		mo, me/ sm, ab, s	sb	cl-lo
$BA_2k_4$	0.18-0.32	2.5YR 3/3		mo, me/ sm, ab		cl-lo
$Bt_1k_5$	0.32-0.43	2.5YR 3/2		st, gr/ me, ab	co, mo	cl-lo
$Bt_2k_6$	0.43-0.57	2.5YR 3/4		mo, me, ab	co, mo	cl
BCk <sub>7</sub>	0.57-0.70	2.5YR 3/4		wk, sm/vsm, ab		cl

<sup>(1)</sup> st: strong, mo: moderate, wk: weak, sm: small, me: medium, vsm: very small, lg: large, and sg: simple grain, ab: angular block, sb: subangular block, gr: granular, pr: prismatic; (2) co: common, mo: moderate; (3) lo: loam; si-cl-lo: silty clay loam; si-lo: silty loam; cl-lo: clay loam; cl: clay; si-cl: silty clay.



as established by the SiBCS (Santos et al., 2013a). However, the possible association with sediment layering during limestone formation is a more plausible explanation. Likewise, the use of a silt/clay ratio above 0.6 to indicate low weathering (Santos et al., 2013a) is not an adequate criterion in soils formed from sedimentary rocks and sediments. As suggested by Shinzato (1998), this ratio may result from sediment weathering rather than the pedogenic process.

All the profiles showed an unusually low degree of flocculation (DF), along with high contents of exchangeable Ca and pH (Table 4). Nevertheless, the findings corroborate calcareous soil data from the Serra da Bodoquena, MS (Pereira et al., 2013). In a study on soils affected by limestone sediments in floodplains in Sousa, Paraíba, Brazil, Corrêa et al. (2003) suggested that a low DF is associated with high Mg<sup>2+</sup> and Na<sup>+</sup> content in the soil, in addition to the presence of expanding 2:1 clay minerals. Marques et al. (2014) attribute the high clay contents in water to high Mg<sup>2+</sup> contents in the sorptive complex.

The P1 and P2 reaction class was neutral, while in P3 and P4, it was moderately acid, ranging from 6.02 to 6.74 (Table 4). The negative values of  $\Delta$ pH indicate the dominance of negative charges in all soil profiles. The most significant ion in the

Table 3. Physical properties of soil profiles in a toposequence in Lavandeira, TO, Brazil

Horizon	Donth	Sar	nd <sup>(1)</sup>	Silt	Clay	NC <sup>(2)</sup>	<b>DF</b> <sup>(3)</sup>	Si/Cl <sup>(4)</sup>	CS/FS <sup>(5)</sup>
HOTIZOII	Depth	CS	FS	Siit	Clay	NC	DF	SI/CI	C5/F5
	cm			g kg <sup>-1</sup>			%		
		Chern	ossolo Rêndz	zico Lítico típ	ico (Lithic Ha	aplustolls) - P	1		
Ak	0.00-0.08	230	90	370	310	170	45	1.19	2.6
ACrk	0.08-0.25	210	90	390	310	220	29	1.26	2.3
	Cami	bissolo Hápli	ico Ta Eutrófi	co léptico hip	oocarbonátic	o (Lithic Hap	lustolls) - P2		
$Ak_1$	0.00-0.05	160	140	380	320	170	47	1.19	1.1
ABk <sub>2</sub>	0.05-0.10	100	110	480	310	140	55	1.55	0.9
BAk <sub>3</sub>	0.10-0.18	180	190	310	320	260	19	0.97	0.9
Bik <sub>4</sub>	0.18-0.31	90	100	490	320	210	34	1.53	0.9
Ck <sub>6</sub>	0.31-0.46	100	80	530	290	250	14	1.83	1.3
		Cambisso	olo Háplico Ca	arbonático lé	ptico (Lithic	Haplustepts)	- P3		
$Ak_1$	0.00-0.05	150	190	290	370	280	24	0.78	0.8
$AB\overline{k}$	0.05-0.10	130	180	290	400	270	33	0.73	0.7
Bik <sub>2</sub>	0.10-0.33	110	160	300	430	300	30	0.70	0.7
		Luvi	ssolo Háplico	Órtico típico	(Typic Rhod	lustalfs) - P4			
Apk <sub>1</sub>	0.00-0.08	140	200	370	290	250	14	1.28	0.7
ABk <sub>2</sub>	0.08-0.13	150	190	330	330	240	27	1.00	0.8
$BA_1k_3$	0.13-0.18	120	180	330	370	280	24	0.89	0.7
$BA_2k_4$	0.18-0.32	120	170	390	320	300	6	1.22	0.7
$Bt_1k_5$	0.32-0.43	120	150	350	380	370	3	0.92	0.8
$Bt_2k_6$	0.43-0.57	90	80	360	470	430	9	0.77	1.1
BCk <sub>7</sub>	0.57-0.70	90	120	270	520	500	4	0.52	8.0

<sup>(1)</sup> FS: fine sand, CS: coarse sand; (2) NC: natural clay; (3) DF: degree of flocculation; (4) Si/CI: silt/clay ratio; (5) CS/FS ratio.



sorptive complex throughout the profiles was Ca<sup>2+</sup> (4.8 to 27.4 cmol<sub>c</sub> kg<sup>-1</sup>), followed by Mg<sup>2+</sup> (5.3 to 11.1 cmol<sub>c</sub> kg<sup>-1</sup>), K<sup>+</sup>, and Na<sup>+</sup> (maximum of 0.3 and 0.04 cmol<sub>c</sub> kg<sup>-1</sup>, respectively). This is in line with studies on calcareous soils in other regions of Brazil (Cunha and Ribeiro, 1998; Ferreira, 2013; Silva, 2013). Unlike the present study, Marques et al. (2014) describe soils with a sorptive complex, where Mg<sup>2+</sup> contents are higher than those of Ca<sup>2+</sup>. Exchangeable Al (Al<sup>3+</sup>) contents were close to zero (Table 4), and pH values were high. A similar pattern was observed in a study on Paleosols in karstic environments of the Bambuí Group (Vasconcelos et al., 2013). Phosphorus contents were low in all the profiles, as also observed in Lagoa Santa Carste (Shinzato, 1998) and Serra da Bodoquena (Silva et al., 2013).

Sum of bases ranged from 11.62 to 36.57 cmol<sub>c</sub> kg<sup>-1</sup>, and base saturation was above 90 %, demonstrating the euthrophic character of the soils (Santos et al., 2013a). Cation exchange capacity at pH 7 ranged from 13.13 to 27.88 cmol<sub>c</sub> kg<sup>-1</sup>. The clay fraction of all the profiles showed CEC above 27 cmol<sub>c</sub> kg<sup>-1</sup>, and corroborating mineralogical data indicates high clay activity (Santos et al., 2013a). These results are in accordance with a study on calcic horizons in Northeast Jordan (Khresat, 2001). CTC

Table 4. Chemical properties of soil profiles in a toposequence in Lavandeira, TO, Brazil

Horizon	OC <sup>(1)</sup>	р	Н	- <b>Δ</b> p <b>H</b> <sup>(2)</sup>	Ca <sup>2+</sup>	Mq <sup>2+</sup>	K⁺	Na⁺	SB	Al <sup>3+</sup>	H⁺	<b>T</b> <sup>(3)</sup>	<b>V</b> <sup>(4)</sup>	<b>P</b> <sup>(5)</sup>	CaCO <sub>3</sub> <sup>(6)</sup>
HOMZON	OC .	H <sub>2</sub> O	KCI	- Дрп.	Ca	Mg	K	Nd	30	AI .	п	•	V		CaCO <sub>3</sub>
	g kg <sup>-1</sup>							– cmol	kg <sup>-1</sup> —				%	mg kg <sup>-1</sup>	g kg <sup>-1</sup>
	Chernossolo Rêndzico Lítico típico (Lithic Haplustolls) - P1														
Αk̄	74.6	7.30	6.55	-0.75	27.4	8.8	0.33	0.04	36.57	0.05	1.19	37.8	97	8	209.20
ACrk	40.8	7.48	6.58	-0.90	19.9	11.1	0.13	0.04	31.17	0.05	1.19	32.4	96	4	102.92
		Ca	mbisso	lo Háplico	o Ta Eut	rófico lé	éptico hi	pocarb	onático (	(Lithic I	Haplust	olls) - F	2		
Ak <sub>1</sub>	45.5	7.15	6.38	-0.77	18.3	7.3	0.18	0.04	25.82	0.05	2.01	27.9	93	5	94.52
ABk <sub>2</sub>	40.8	7.07	6.25	-0.82	14.6	10.9	0.11	0.02	25.63	0.05	2.01	27.7	93	3	94.52
BAk <sub>3</sub>	28.2	7.18	6.22	-0.96	13.7	7.5	0.05	0.02	21.27	0.05	1.19	22.5	95	2	79.41
Bik <sub>4</sub>	31.9	7.34	6.16	-1.18	14.0	7.7	0.05	0.03	21.78	0.05	2.01	23.8	91	3	91.17
Ck <sub>5</sub>	37.0	7.00	6.15	-0.85	14.5	7.2	0.05	0.04	21.79	0.05	2.01	23.9	91	5	96.20
			Ca	mbissolo	Háplic	o Carbo	nático le	éptico (	Lithic Ha	pluste	pts) - P	3			
$Ak_1$	25.9	6.02	4.84	-1.18	5.8	6.4	0.30	0.02	12.52	0.05	3.66	16.2	77	3	87.81
$AB\overline{k}$	22.7	6.28	4.80	-1.48	6.5	5.6	0.25	0.02	12.37	0.05	2.01	14.4	86	2	220.56
Bik <sub>2</sub>	13.4	6.72	5.45	-1.27	6.0	5.5	0.10	0.02	11.62	0.05	2.01	13.7	85	2	81.09
				Luviss	olo Háp	olico Órt	ico típic	o (Typic	Rhodus	stalfs) -	P4				
Apk <sub>1</sub>	24.9	6.42	5.00	-1.42	6.3	9.2	0.14	0.02	15.66	0.05	2.84	18.5	84	4	81.09
ABk <sub>2</sub>	27.8	6.06	4.86	-1.2	7.8	6.9	0.11	0.02	14.83	0.05	2.84	17.7	84	3	81.09
$BA_1k_3$	20.4	6.18	4.86	-1.32	6.3	6.7	0.09	0.02	13.11	0.05	2.01	15.2	86	3	81.09
$BA_2k_4$	18.9	6.17	4.93	-1.24	7.5	5.3	0.09	0.02	12.91	0.05	2.01	15.0	86	3	79.41
Bt <sub>1</sub> k <sub>5</sub>	12.8	6.11	4.94	-1.17	5.1	9.4	0.07	0.02	14.59	0.05	1.19	15.8	92	2	79.41
Bt <sub>2</sub> k <sub>6</sub>	8.4	6.74	5.28	-1.46	4.8	7.0	0.06	0.03	11.89	0.05	1.19	13.1	91	2	81.09
BCk <sub>7</sub>	7.2	6.52	5.41	-1.11	5.7	6.1	0.09	0.04	11.93	0.05	1.19	13.2	91	2	82.77

<sup>(1)</sup> OC: total organic carbon; (2) ΔpH: pH in KCI - pH in water; (3) T: cation exchange capacity, pH 7.0; (4) V: base saturation; (5) P: available phosphorus, extractor Olsen; (6) CaCO<sub>3</sub>: calcium carbonate equivalent.



Calcium carbonate ( $CaCO_3$ ) contents ranged from 79.41 to 220.56 g kg<sup>-1</sup> (Table 4), with the highest values found in the  $A\bar{k}$  horizon of P1 (209.2 g kg<sup>-1</sup>) and the  $AB\bar{k}$  horizon of P3 (220.56 g kg<sup>-1</sup>), both soils showing lithic contact up to a depth of 0.30 m. These results are explained by weathering of the parent material, which releases ions that become soluble, and restricted drainage caused by proximity to rock, which hinders ion leaching in the solution, leading to the accumulation of secondary  $CaCO_3$ , primarily in the soil layer immediately above.

In a study on soils formed from limestone in the Serra da Bodoquena, MS, Pereira et al. (2013) attributed the lower CaCO<sub>3</sub> contents to good drainage, which favored bicarbonate solubilizing and leaching. They found higher CaCO<sub>3</sub> contents in the soils in lower areas, which they explained as the influx of ions from higher elevations and reduction of losses due to restricted drainage. In calcic horizons in Jordan, Khresat (2001) found an accumulation of secondary carbonate calcium at lower elevations, in contrast to the present study, where parent material was the determinant factor for CaCO<sub>3</sub>, which served as a carbonate source and structural control, restricting drainage.

# Carbon and humic fractions of organic matter

Surface horizons showed higher contents of organic carbon - OC (7.2 to 50.7 g kg<sup>-1</sup>), which decreased with depth (Table 5). Distribution of the humic fraction followed the pattern observed for OC. Organic carbon contents were 1.4 to 8.2 g kg<sup>-1</sup> in the fulvic acid fraction (C-FAF), 0.5 to 13.1 g kg<sup>-1</sup> in the humic acid fraction (C-HAF), and 5.1 to 38.2 g kg<sup>-1</sup> in humin. C-FAF represented the lowest portion of the fractions, followed by C-HAF. Both fractions correspond to the soluble portion in the alkaline extract (AE) and exhibit higher chemical reactivity (Benites et al., 2003). Soil C was mostly concentrated in humin, corroborating studies on humic substances of calcareous soils (Volkoff, 1980; Ferreira, 2013). The authors attribute the predominance of humin to its high stability and polymerization, which results from its close interaction with the mineral fraction of the soil (Duchaufour, 1970; Cunha and Ribeiro, 1998; Pereira et al., 2013).

The alkaline extract (AE), which is the sum of C-FAF and C-HAF, ranged from 2.6 to 16.7 g kg<sup>-1</sup> along the toposequence, varying among the horizons in relation to C content. Similar results were found in calcareous soils from Irecê, Bahia, Brazil (Cunha and Ribeiro, 1998). The C-HAF/C-FAF ratio ranged from 0.1 to 6.4, with the widest amplitude recorded in P2 and P4 (Table 5). The wide range indicates C mobility throughout the profiles and, as a result, loss of the most soluble fraction (C-FAF) (Volkoff et al., 1984). The values of the AE/humin ratio ranged from 0.1 to 0.6 (Table 5), indicating high organic matter stability. This was also observed in earlier studies on organic fractions in calcareous soils (Fontana et al., 2010; Pereira et al., 2013).

Organic matter stability was described by Duchaufour (1970), who stated that the close relationship between organic matter and 2:1 clays is promoted by Ca and Fe ions. This was corroborated by other authors (Fanning and Fanning, 1989; Bockheim and Gennadiyev, 2000; Kämpf and Curi, 2012), who report that the interactions between organic and mineral fractions are key factors in determining the dark color of chernozemic horizons. Other studies are more specific, suggesting that organic matter stability in calcareous soils results from the 2:1 clay mineral and Ca<sup>2+</sup> and Mg<sup>2+</sup> ion interactions with ionized carboxylic acid and hydroxide groups (Duchaufour, 1976; Cunha and Ribeiro, 1998; Corrêa et al., 2003; Pereira et al., 2013; Silva, 2013).

#### Weathering complexes and selective Fe dissolution (Fes, Fed, and Feo)

Along the toposequence, the main oxide in the ADFE was  $SiO_2$  (123.7 to 219.3 g kg<sup>-1</sup>), followed by  $Fe_2O_3$  (60 to 102 g kg<sup>-1</sup>) (Table 6). In P1 and P2, however,  $Fe_2O_3$  contents were slightly lower than in the other profiles. Profiles P1 and P2 were characterized by thinner soil horizons, with high organic matter content, which increases moisture



Table 5. Chemical fractioning of organic matter of soils in a toposequence in Lavandeira, TO, Brazil

Havinan	OC <sup>(1)</sup>	C FAF(2)	C 11AF(3)	C-HUM <sup>(4)</sup>	<b>AE</b> <sup>(5)</sup>	C-FAF	CHAE	11111111	C-HAF	AE	AE
Horizon	OC.	C-FAF	С-паг	С-ном	AE	C-FAF	C-HAF	HUM	C-FAF	ОС	Hum
		g l	κg <sup>-1</sup> ———			(	% ———				
			Chernos	solo Rêndzio	o Lítico tí	<i>pico</i> (Lithic	Haplustolls	s) - P1			
Αk̄	50.7	2.7	5.4	38.2	8.1	5.3	10.7	75.3	2.0	0.2	0.2
ACrk	40.8	8.2	0.5	35.1	8.7	20.1	1.2	86.0	0.1	0.2	0.2
		Cambiss	olo Háplico	Ta Eutrófico	léptico h	ipocarbona	<i>ático</i> (Lithic	Haplustol	ls) - P2		
$Ak_1$	45.5	5.6	8.8	33.9	14.4	12.3	19.3	74.5	1.6	0.3	0.3
ABk <sub>2</sub>	40.8	3.1	6.7	33.7	9.8	7.6	16.4	82.6	2.2	0.2	0.2
BAk <sub>3</sub>	28.2	2.7	3.6	21.9	6.3	9.6	12.8	77.7	1.3	0.2	0.2
Bik <sub>4</sub>	33.8	2.6	7.5	28.6	10.1	7.7	22.2	84.6	2.9	0.3	0.3
Ck <sub>5</sub>	37.9	2.8	12.9	28.0	15.7	7.4	34.0	73.9	4.6	0.4	0.4
		C	Cambissolo	Háplico Carl	bonático l	<i>éptico</i> (Lith	nic Haplust	epts) - P3			
$Ak_1$	25.9	2.0	12.7	16.5	14.7	7.7	49.0	63.7	6.4	0.6	0.6
$AB\overline{k}$	22.7	2.6	10.8	15.4	13.4	11.5	47.6	67.8	4.2	0.6	0.6
Bik <sub>2</sub>	13.4	2.1	3.4	9.3	5.5	15.7	25.4	69.4	1.6	0.4	0.4
			Luvisso	olo Háplico Ć	Prtico típio	o (Typic Ri	nodustalfs)	- P4			
Apk <sub>1</sub>	24.9	2.8	12.2	17.5	15.0	11.2	49.0	70.3	4.4	0.6	0.6
$ABk_2$	27.8	3.6	13.1	17.0	16.7	12.9	47.1	61.2	3.6	0.6	0.6
$BA_1k_3$	20.4	4.0	8.5	14.2	12.5	19.6	41.7	69.6	2.1	0.6	0.6
$BA_2k_4$	18.9	2.8	8.8	12.1	11.6	14.8	46.6	64.0	3.1	0.6	0.6
Bt <sub>1</sub> k <sub>5</sub>	13.2	1.9	4.2	9.8	6.1	14.4	31.8	74.2	2.2	0.5	0.5
$Bt_2k_6$	9.3	1.4	1.3	7.7	2.7	15.1	14.0	82.8	0.9	0.3	0.3
BCk <sub>7</sub>	7.2	1.9	0.7	5.1	2.6	26.4	9.7	70.8	0.4	0.4	0.4

<sup>(1)</sup> C: total organic carbon; (2) C-FAF: organic carbon in the fulvic acid fraction; (3) C-HAF: organic carbon in the humic acid fraction; (4) C-HUM: organic carbon in the humin fraction; (5) FAF, HAF, HUM (humin), and AE (alkaline extract): relationship of each fraction in relation to total organic carbon.

retention and likely promotes Fe reduction, complexation, and removal from the system (Corrêa et al., 2003). The contents of  $Fe_2O_3$ ,  $TiO_2$ , and  $P_2O_5$  were low, reflecting the nature of the parent material. Similarly, Fe oxide and Ti contents are in line with values described for calcareous soils in Serra da Bodoquena, MS (Pereira et al., 2013; Silva, 2013).

The molecular relationships ki (1.91 to 3.10) and kr (1.34 to 2.10) indicate that the soils underwent moderate to intense weathering. This is confirmed by the mineralogy of the clay fraction, particularly the occurrence of hydroxyl interlayered (HI) vermiculite and illite in P1, P2, and P3, and kaolinite in P4 (footslope). All the profiles exhibited higher  $SiO_2$  than  $Al_2O_3$  contents, and the higher ki values indicate low silica solubilization and removal in the profile, with consequent formation of 2:1 clay minerals. In the subsurface horizons of calcareous soils in Serra da Bodoquena, Silva et al. (2013) attributed ki values from 1.96 to 2.56 to the occurrence of 2:1 clay minerals. Similarly, Shinzato (1998) observed a ki from 2.3 to 4.2 in soils from Lagoa Santa Carste, MG, due to dominance of 2:1 clay minerals.

The results for P3 (ki = 1.91 to 2.2; kr = 1.37 to 1.5) and P4 (ki = 2.03 to 2.20; kr = 1.37 to 1.54) are associated with previous processes in the parent material. The sediments might have already been weathered when they were deposited on the backslope and footslope.



**Table 6.** Chemical composition and ki and kr molecular relationship for soil profiles in a toposequence in Lavandeira, TO, Brazil

Horizon	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	ki <sup>(1)</sup>	kr <sup>(2)</sup>	Al <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>			
			— g kg <sup>-1</sup> —								
	Chernossolo Rêndzico Lítico típico(Lithic Haplustolls) - P1										
$A\overline{k}$	168.5	92.9	67.7	6.36	2.80	3.08	2.07	2.16			
ACrk	160.1	87.7	65.6	5.68	2.80	3.10	2.10	2.10			
Cambissolo Háplico Ta Eutrófico léptico hipocarbonático (Lithic Haplustolls) - P2											
$Ak_1$	152.1	80.5	60.0	4.04	2.65	3.21	2.18	2.11			
$ABk_2$	157.9	95.0	72.4	4.99	2.60	2.83	1.90	2.06			
BAk <sub>3</sub>	167.3	110.6	74.4	4.98	2.30	2.57	1.80	2.34			
$Bik_4$	163.8	97.4	72.3	6.77	2.30	2.86	1.94	2.12			
Ck <sub>5</sub>	163.9	94.4	67.8	4.96	2.45	2.95	2.02	2.18			
	Can	nbissolo Há	plico Carbo	onático lép	otico (Lithi	c Hapluste	epts) - P3				
$Ak_1$	150.4	123.1	90.4	5.60	0.69	2.08	1.41	2.14			
$AB\overline{k}$	157.8	125.2	83.9	5.58	0.73	2.14	1.50	2.34			
Bik <sub>2</sub>	178.2	159.0	96.1	6.94	0.65	1.91	1.37	2.60			
		Luvissolo	Háplico Ór	tico típico	(Typic Rho	odustalfs)	- P4				
$Apk_1$	123.7	103.6	77.2	7.87	0.68	2.03	1.37	2.11			
$ABk_2$	134.6	104.0	80.6	5.34	0.62	2.20	1.47	2.03			
$BA_1k_3$	133.0	111.5	83.4	8.40	0.55	2.03	1.37	2.10			
$BA_2k_4$	150.2	116.9	87.6	5.99	0.55	2.18	1.48	2.09			
Bt <sub>1</sub> k <sub>5</sub>	175.2	137.7	88.6	5.55	0.51	2.16	1.53	2.44			
$Bt_2k_6$	205.7	169.0	101.9	6.22	0.45	2.07	1.49	2.60			
BCk <sub>7</sub>	219.3	176.8	102.0	6.22	0.42	2.11	1.54	2.72			

<sup>(1)</sup> ki:  $(SiO_2/AI_2O_3) \times 1.7$ ; (2) kr:  $(SiO_2 \times 1.7)/[AI_2O_3 + (0.64 \times Fe_2O_3)]$ .

With regards to selective Fe dissolution (Fes, Fed, and Feo), the most important fractions in all the profiles were Fed and Fes. A similar result was described for calcareous soils in Chapada do Apodi, Ceará, Brazil (Ferreira, 2013). Fed contents ranged from 9.53 to 29.11 g kg<sup>-1</sup> (Table 7), confirming the low Fe level in the parent material. In an earlier study on calcareous soils in Irecê, Bahia, Cunha et al. (1999) attributed Fed values from 14.59 to 27.25 g kg<sup>-1</sup> to the nature of the parent material. Moreover, a low Fe/clay relationship (0.05 to 0.12) reinforces the poor Fe participation in this fraction (Pereira and Anjos, 1999). This pattern is consistent with the low Fes value and can be credited to low Fe content in the parent material. The Feo/Fed ratio reflects the dominance of oxide forms with low crystallinity and is usually higher in surface horizons, associated with higher organic carbon (Kämpf and Schwertmann, 1983; Anjos et al., 2007). Fe complexation by functional groups of organic matter decreases the crystallinity of pedogenic Fe oxides (Anjos et al., 2007).

The  $Bt_2k_6$  horizon of P4 contained 9.46 g  $kg^{-1}$  Feo, and the  $Bt_1k_5$  horizon, 6.70 g  $kg^{-1}$ . Some of the poorly crystalline Fe oxides were likely moved from the upper horizons. The Fed/Fes ratio ranged from 0.2 to 0.45, with the lowest value in P1. These results suggest that Fe was mostly associated with other groups of minerals, especially illite. This finding is corroborated by clay mineralogy.



# Mineralogy of sand and clay fractions

The mineralogy of fine and coarse sand showed predominance of quartz (Table 8), a mineral with high weathering resistance. In fact, quartz is dominant in the sand fraction of a significant part of Brazilian soils (Shinzato, 1998; Miranda and Ferreira, 1999; Alencar, 2002; Anjos et al., 2007; Silva, 2013; Vasconcelos et al., 2013). The mineralogy of the sand fraction was uniform, with a variation in crystallinity. Poorly crystalline quartz was found in P1 and P2, likely because of lower silica content resulting from weathering. Other studies report silica predominance in the sand fraction of calcareous soils (Ferreira, 2013; Pereira et al., 2013; Silva et al., 2013), a situation frequently observed in soils from the Bambuí Group (Embrapa, 1983).

In P1, P2, and P3, HI-vermiculite was found in the clay fraction, followed by illite, kaolinite, and quartz (Table 8). The reflections of samples subjected to the heating pretreatment tended to merge, suggesting the presence of vermiculite interlayered with Al hydroxide polymers. Although inter-stratified vermiculite is commonly found in wet and cold environments (Boero et al., 1992), it has been identified in Brazilian soils under different conditions (Anjos et al., 2007). According to this last author, alternate periods of intense rainfall and prolonged dry weather in Maranhão, Brazil, located in the equatorial region,

Table 7. Iron forms (Fes, Fed and Feo) in soil profiles in a toposequence in Lavandeira, TO, Brazil

Horizon	Feo <sup>(1)</sup>	Fed <sup>(1)</sup>	Fes <sup>(1)</sup>	Fed/Clay	Fes/Clay	Feo/Fed	Fed/Fes					
		— g kg <sup>-1</sup> —										
	Chern	ossolo Rênd	Izico Lítico	<i>típico</i> (Lithic	Haplustolls)	- P1						
$A\overline{k}$	5.79	9.53	47.34	0.06	0.28	0.61	0.20					
ACrk	4.68	13.06	45.87	0.06	0.21	0.36	0.28					
Caml	Cambissolo Háplico Ta Eutrófico léptico hipocarbonático (Lithic Haplustolls) - P2											
$Ak_1$	6.11	14.17	41.96	0.08	0.25	0.43	0.34					
$ABk_2$	5.85	16.36	50.63	0.12	0.36	0.36	0.32					
BAk <sub>3</sub>	5.47	16.11	52.03	0.06	0.20	0.34	0.31					
Bik <sub>4</sub>	7.22	14.18	50.56	0.07	0.24	0.51	0.28					
Ck <sub>5</sub>	7.11	13.54	47.41	0.05	0.19	0.53	0.29					
	Cambissolo Háplico Carbonático léptico (Lithic Haplustepts) - P3											
$Ak_1$	7.16	26.75	63.22	0.10	0.23	0.27	0.42					
$AB\overline{k}$	8.16	21.73	58.67	0.08	0.22	0.38	0.37					
Bik <sub>2</sub>	7.35	27.21	67.20	0.09	0.22	0.27	0.40					
	Luvi	ssolo Háplic	o Órtico típ	ico (Typic Rh	odustalfs) -	P4						
Apk <sub>1</sub>	7.64	14.49	53.99	0.06	0.22	0.53	0.27					
$ABk_2$	8.48	21.93	56.36	0.09	0.23	0.39	0.39					
$BA_1k_3$	7.72	20.75	58.32	0.07	0.21	0.37	0.36					
$BA_2k_4$	7.17	27.71	61.26	0.09	0.20	0.26	0.45					
Bt <sub>1</sub> k <sub>5</sub>	6.70	24.46	61.96	0.06	0.16	0.27	0.39					
$Bt_2k_6$	9.46	25.13	71.26	0.06	0.17	0.38	0.35					
BCk <sub>7</sub>	8.60	29.11	71.33	0.06	0.14	0.30	0.41					

<sup>&</sup>lt;sup>(1)</sup> Feo: Fe extracted by acid ammonium oxalate; <sup>(2)</sup> Fed: Fe extracted by dithionite citrate bicarbonate; <sup>(3)</sup> Fes: Fe determination by sulfuric acid digestion ( $Fe_2O_3$ ).



**Table 8.** Mineralogy of sand and clay fractions of selected horizons

	Horizon	Mineralogy	Mineralogy								
Profile		Clay	Coarse sand	Fine sand							
P1	ACrk	vermiculite HE>> illite, kaolinite, quartz	quartz	quartz							
P2	Bik <sub>4</sub>	vermiculite HE>> illite, kaolinite, quartz	quartz	quartz							
Р3	Bik <sub>2</sub>	vermiculite HE>> illite, kaolinite, quartz	quartz	quartz							
P4	Bt <sub>1</sub> k <sub>5</sub>	Kaolinite>> quartz	quartz	quartz							

preserves high activity clay minerals due to internal restriction to drainage, a condition that leads to the occurrence of minerals such as smectite and HI-vermiculite. It is important to underscore that the AI between the layers destabilizes vermiculite (Resende et al., 2005), making it more susceptible to transformation.

In P4, the well-defined kaolinite reflections suggest its dominance (Shinzato, 1998; Cunha and Ribeiro, 1998). Kaolinite may originate from the transformation of primary and/or secondary minerals or by neoformation through recombination of Si in solution. In a study on calcareous soils in Sardinia, Boero et al. (1992) identified illite and kaolinite minerals as the main constituents of the clay fraction, whereas in northwest Italy they observed vermiculite with Al hydroxide between the layers. In studies of soils in the Mediterranean region, Durn (2003) found a predominance of illite and kaolinite in the clay fraction.

# Soil genesis and classification

The variation in soil properties along the toposequence was closely associated with the topography factor, which determines drainage and surface runoff. In addition, the parent material consisted primarily of weathered limestone, and after topography, it was an important factor in soil genesis, where the profiles were of allochthonous and autochthonous origin. Accordingly, Pereira et al. (2013), highlights topography as one of the main determinants of the genesis of calcareous soils in Serra da Boodoquena, MS.

Evidence of the pedogenic process of melanization in surface horizons of the profiles varied in intensity, and the darker colors resulted from the interaction of the mineral fraction with the functional groups of organic matter (Duchaufour, 1970; Arnold, 1983; Fanning and Fanning, 1989; Bockheim and Gennadiyev, 2000; Kämpf and Curi, 2012). The presence of  $CaCO_3$  in the profiles may be evidence of calcification or that the  $CaCO_3$  was inherited from the parent material. Sources of  $Ca^{2+}$  and  $CO_3^{2-}$  are required for  $CaCO_3$  precipitation and pedogenic formation of carbonates and bicarbonates. The designation of horizons varies according to the carbonate source, and the " $\overline{k}$ " suffix is used for secondary carbonates, where "k" indicates carbonates derived from the parent material (Santos et al., 2013b).

Evidence of eluviation and illuviation were observed in P4 (Kämpf and Curi, 2012), such as the occurrence of common and moderate clay skins in the  $Bt_1k_5$  and  $Bt_2k_6$  horizons, followed by an increase in clay in the  $Bt_2k_6$  horizon, both indications of clay translocation.

With respect to soil classification, due to organic carbon content below 80 g kg<sup>-1</sup> and the fact that upper horizons did not meet SiBCS criteria for other horizon types, the surface diagnostic horizons of P2, P3, and P4 were identified as moderate A. In contrast, P1 met the requirements for classification as *A chernozêmico* (Santos et al., 2013a). With respect to subsurface diagnostic horizons, P2 and P3 did not show a noticeably pedogenic process, i.e., they exhibited low pedogenic evolution. The subsurface horizons of P2 and P3 were thus classified as incipient B (Santos et al., 2013b). The pattern of clay skins, along with texture and structure, were sufficient to classify the subsurface horizon of P4



as textural B (Santos et al., 2013b). P1 did not show a subsurface diagnostic horizon. However, an AC transitional horizon was observed and identified using the suffix "r", indicating slightly altered rock. The "r" suffix is exclusively for C horizons (Santos et al., 2013b), but in this profile, it was used for the transitional horizon. The suffix "k" was used in the horizons of all profiles to indicate the presence of  $CaCO_3$  inherited from the parent material. A number of horizons, however, were enriched with secondary  $CaCO_3$  and identified by the suffix "k", according to Santos et al. (2013b).

The soil order of P1 was classified in the SiBCS (Santos et al., 2013a) as a *Chernossolo* (equivalent to Mollisols) due to the lithic contact and more than 150 g kg $^{-1}$  of CaCO $_3$  equivalent in the A horizon, which was identified as *chernozêmico* (Santos et al., 2013a). In the suborder level, it met the criteria of *rêndzico*, due to the carbonate content and parent material (Santos et al., 2013a); the Great Group was *lítico* (lithic), due to the contact with limestone up to a depth of 0.50 m; and the subgroup was *típico* (typic). P1 was classified by the SiBCS criteria as a *Chernossolo Rêndzico Lítico típico*. According to Soil Taxonomy (Soil Survey Staff, 2014), the mollic epipedon directly above the rock and the dry climate, which indicates an ustic soil moisture regime, resulted in its being classified as an Ustolls. The lithic contact up to a depth of 0.50 m and lack of any diagnostic subsurface horizon identified P1 as a Lithic Haplustolls.

The soil order of P2 and P3 was classified as a Cambissolo (equivalent to an Inceptisol) owing to the incipient diagnostic horizon. At the suborder level they were classified as háplico (haplic) because of the absence of a distinguishing trait that would characterize them as another suborder. At the Great Group level, P2 was identified as Ta eutrófico, due to high clay activity and base saturation. Since the CaCO<sub>3</sub> content was between 50 and 150 g kg<sup>-1</sup>, and the profile had lithic contact from 0.50 to 1.00 m from the soil surface, P2 was classified at the subgroup level as léptico hipocarbonático. In the SiBCS, P2 was classified as a Cambissolo Háplico Ta Eutrófico léptico hipocarbonático. In Soil Taxonomy (Soil Survey Staff, 2014), the concept of epipedon "may include part or all of an illuvial B horizon if the darkening by organic matter extends from the soil surface into or through the B horizon"; thus, surface horizons, including Ak<sub>1</sub>, ABk<sub>2</sub>, and BAk<sub>3</sub>, with total thickness of 0.18 m, are qualified as mollic epipedon. Since base saturation ranges from 91 to 95 %, the profile was classified as a Mollisol. Considering the local dry climate, cambic horizon, and shallow profile (A + B of 0.33 m), the profile was classified as a Haplustolls; at the subgroup level, the lithic contact at up to 0.50 m from the mineral soil surface identified P2 as a Lithic Haplustolls.

Profile P3 showed a  $CaCO_3$  content of 220 g kg<sup>-1</sup> in the ABk horizon, which characterizes it as *carbonático* (carbonatic), and at the subgroup level, the lithic contact between 0.50 and 1.00 m defines it as *léptico* (leptic). Therefore, in the SiBCS, P3 was classified as a *Cambissolo Háplico Carbonático léptico*. According to Soil Taxonomy, the color and thickness of the epipedon characterizes an ochric surface horizon, which associated with the cambic horizon and dry climate, identified P3 as an Ustepts. Although ABk had high  $CaCO_3$  equivalent content (220.56 g kg<sup>-1</sup>), it was less than 0.15 m thick, not qualifying as a calcic horizon, and the lithic contact at 0.33 m classified P3 as a Lithic Haplustepts.

Profile P4 was classified as a *Luvissolo* (corresponding to an Alfisol) due to the diagnostic B textural horizon being associated with high-activity clay and base saturation. At the suborder level it was identified as  $h\acute{a}plico$  (haplic), and due to the shallow profile (A + B equal to 0.57 m), the Great Group was órtico (orthic). However, the high CaCO<sub>3</sub> content (79.41 to 82.77 g kg<sup>-1</sup>) that meets the requirement for *hipocarbonático* (Santos et al., 2013a) should be considered in the classification of this profile, since it is a relevant feature for management purposes, affecting parameters such as pH, available P, and soil micronutrient dynamics. Profile P4 was thus classified as a *Luvissolo Háplico Órtico típico* and a new class is proposed,



Luvissolo Háplico Órtico hipocarbonático, with criteria similar to other subgroups with the same characteristics. In Soil Taxonomy, the epipedon is ochric due to the  $Apk_1$  color (5YR 4/4), the subsurface horizon is argillic, and the high base saturation and dry climate identify P4 as Ustalfs at the suborder level. In the lower half of the argillic horizon, the hue of 2.5YR, a moist value of 3, and chroma of 4 defined the profile as Rhodustalfs. Given the absence of detailed information on the variation of the soil moisture regime, the C2wA'a' climate classified P4 as a Typic Rhodustalfs.

## **CONCLUSIONS**

Soil variations in the toposequence, particularly in profile depth and horizon development, were determined by topography, which governed drainage and surface runoff. Secondarily, the parent material affected soil morphology, texture, and chemical properties. All profiles showed high silt and clay content, high Ca and Mg contents, high pH, and low exchangeable Al. Base saturation and calcium carbonate equivalent were also high, and the horizons showed dark color due to high organic matter, dominated by the humin fraction.

Profiles were classified according to the SiBCS and Soil Taxonomy, and the main difference at the soil order level was for P2, classified as a *Cambissolo* and Mollisol, respectively. With regards to the SiBCS, we propose a new subgroup level for *Luvissolos Háplicos Órthicos* which present hypocarbonate features, since a  $CaCO_3$  content above 50 g kg<sup>-1</sup> is of great importance to soil management. Therefore, P4 would be classified as a *Luvissolo Háplico Órtico hipocarbonático*.

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