

Division - Soil in Space and Time | Commission - Soil Survey and Classification

Genesis and Classification of Nitisols from Volcano-Sedimentary Lithology in Northeastern Brazil

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ABSTRACT: On the southern coast of Pernambuco State (PE), Brazil, lithotypes of the Cabo Basin (volcanic and sedimentary rocks), in association with the relief, allow the determination of the dynamics of the formation of *Nitossolos Háplicos* (Nitisols), including those with high levels of exchangeable aluminum. The objective of this study was to evaluate the influence of lithological diversity (basalt and sedimentary siliciclastic rocks) on the morphological, physical, chemical, and mineralogical properties of *Nitossolos Háplicos* along a slope (P1-summit, P2-backslope, P3-footslope) on the southern coast of PE, in order to consider its genesis and the relation of soil properties to adjacent environments and to evaluate its framing within the Brazilian Soil Classification System (SiBCS). The interaction of lithology/soil permeability and climate indicate significant differences in the mineralogical composition and dynamics of soil chemical elements. The profiles P1 and P2 are subject to monosialitization, ferralitization, and alitization processes. All profiles showed high Fe contents (ferric soils) and clay fractions, consisting primarily of kaolinite, goethite, hematite, and gibbsite, as well as quartz and feldspar in the sand and silt fractions. However, smectite minerals (P3) are probably inherited from the sedimentary source material. In the conglomerate samples, under P3, biotite, muscovite, and plagioclase were identified. Allytic characteristics (P3) are probably associated with the weathering of aluminous smectite minerals. These properties distinguish these soils from adjacent *Nitossolos* and other *Nitossolos* in Brazil. For the classification of soils according to SiBCS, considering the high levels of Fe and Al, *Nitossolo Háplico distroférico* (P1 and P2) and *Nitossolo Háplico alitiférico* (P3) are suggested, and according to the World Reference Base of Soils (WRB), the soils are classified as Ferritic Nitisols.

Keywords: smectites, alitic soils, *Nitossolo Háplico*, Nitisols Ferritic.

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INTRODUCTION

The southern part of the Pernambuco coast is part of the Cabo volcanic-sedimentary basin, which is associated with the separation of the South American and the African continents during the Cretaceous. This tectonic event began in the Late Cretaceous, when the deposition of fluvio-deltaic sediments occurred. In the Upper Cretaceous, intense volcanic activity was responsible for the diversity of acid and alkaline rocks found in the basin (Lima Filho et al., 1996). Thus, volcanic rocks, such as basalt, andesite, trachyte, rhyolite, and ignimbrites, integrate the Ipojuca Formation, and the sedimentary rocks, particularly the Cabo Formation, are constituted essentially by conglomerates (originating from granite, gneiss, migmatite, and micaschist) associated with siltstone and argillite (Sial et al., 1987; Mabesoone and Alheiros, 1988; Alheiros and Ferreira, 1989; Nascimento et al., 2009).

According to the soil surveys carried out by Brasil (1972) and Araújo Filho et al. (2000), the main orders of soils that occur along the southern coast of Pernambuco are *Argissolos* (Acrisols; Lixisols), *Latosolos* (Ferralsols), *Nitossolos* (Nitisols), and *Gleissolos* (Gleysols). Previously, studies have been performed in the abovementioned region with *Nitossolos* (Oliveira et al., 2004; Neves et al., 2018), which are always formed from the basaltic alteration of the Ipojuca Formation, classified as *Nitossolo Vermelho* and *Nitossolo Háptico*, typically presenting a kaolinitic and oxidic mineralogy in addition to low levels of exchangeable Al^{3+} .

The *Nitossolos* are composed of mineral material and have a nitic B horizon below the A horizon, with clay of low activity or allytic character in most of the B horizon within 1.50 m from the surface. These soils have a clayey to very clayey texture and a textural gradient equal to or inferior to 1.5. In addition, *Nitossolos* present no marked polychromy (color variation in depth) in the profile (Santos et al., 2013).

Basic and intermediate rocks are widely documented as the parent lithology for soils with a nitic horizon (Cooper and Vidal-Torrado, 2000; Cooper et al., 2010; Melo et al., 2010; Soil Survey Staff, 2014; De Wispelaere et al., 2015). The *Nitossolos* developed from basalt throughout Brazil (Brasil, 1972; Santos Filho et al., 1978; Araújo Filho et al., 2000; Tremocoldi, 2003; Oliveira et al., 2004; Neves et al., 2018) generally present values of Fe_2O_3 (sulfuric digestion) above 18 % and are classified as *Nitossolos Vermelhos* or *Brunos* (Santos et al., 2013). However, for *Nitossolos Hápticos*, neither the ferric nor the allytic character have been predicted to date (Santos et al., 2013).

Due to the distinct lithotypes around the Cabo Basin (volcanic rocks and siliciclastic sedimentary rocks), studies have shown the occurrence of *Argissolos* with high levels of exchangeable Al ($>4 \text{ cmol}_c \text{ kg}^{-1}$) and high clay activity (smectite minerals in the clay fraction), that formed from the weathering of conglomerates (Costa, 2012). Although soils with similar properties have been studied in several parts of Brazil (Cunha et al., 2014, 2015; Delarmelinda et al., 2017), previous pedological studies in the Cabo Basin do not cover the current knowledge of local geological diversity. The presence of smectites is also not common in the clay fraction of the *Nitossolos* in Brazil, probably due to the strong weathering involved in the formation of these soils, predominated by monosialitization and ferralitization processes (Cooper and Vidal-Torrado, 2005).

The southern coast of Pernambuco is inserted in areas of dissected plateaus. In addition to the close relationship between parent material and soil properties (Brilhante et al., 2017; Neves et al., 2018), the relief plays a key role in pedodiversity, since along the slopes, there may be mixtures of parent materials, conditioning the formation of soil with peculiar properties. It is possible to find the occurrence of *Nitossolos* distinct from those previously studied in other regions of Brazil (Cooper and Vidal-Torrado, 2000; Ferreira et al., 2003; Silva et al., 2009; Melo et al., 2010) and from those already studied in this region of Pernambuco (Araújo Filho et al., 2000; Oliveira et al., 2004; Neves et al., 2018).

The southern coastal region of Pernambuco, in addition to the estuarine environments, is formed by the Atlantic forest ecosystem, the natural vegetation of which is practically nonexistent. The area is mainly used for sugarcane cultivation, a large industrial park, and dense urban areas with a population of approximately 500,000 inhabitants (IBGE, 2010). Considering the scarcity of pedological studies in the Cabo Basin region, detailed knowledge of soil diversity and its properties is fundamental for the ecological and socioeconomic sustainability and maintenance of the region. In this context, this study aimed to evaluate the influence of lithological diversity (basalts and siliciclastic sedimentary rocks) along a slope on the morphological, physical, chemical, and mineralogical properties of *Nitossolos Háplicos* in order to understand its genesis, its framing in the Brazilian Soil Classification System (SiBCS), and its enhancement in the SiBCS.

MATERIALS AND METHODS

Study area and sampling

The study area is located in the municipality of Cabo de Santo Agostinho at the southern coast of the state of Pernambuco (Figure 1). The local geology consists of Ipojuca Formation basalt with rare outcrops and conglomerates of the Cabo Formation, with significant outcrops along the area. In the Cabo Formation, besides conglomerates formed by fragments of granite and gneiss, there is also siltstone and argillite, often interspersed between the conglomeratic materials. The relief is predominantly convex and wave-like formed by hills linked to the so-called *Mares de Morros* geomorphology (Assis, 1999).

The climate is hot and humid, type As' (Köppen classification system), with average annual rainfall of 2,200 mm and average temperature of 25 °C (Assis, 1999). The native vegetation is predominantly subperenifolia forest, distributed in the Atlantic Forest

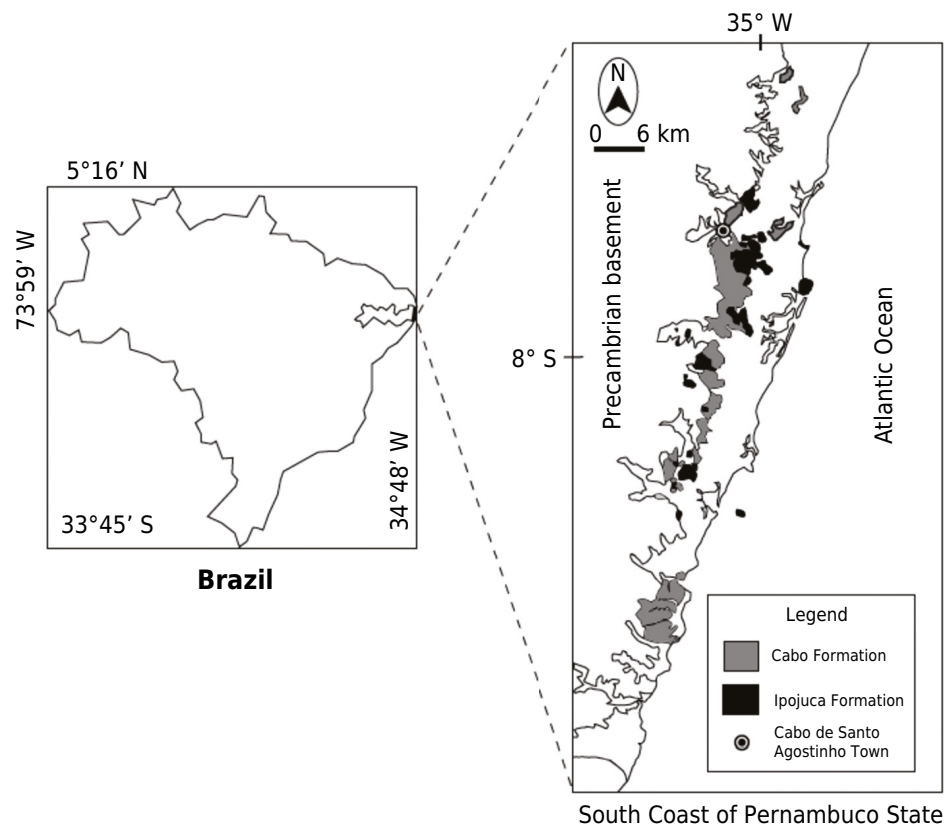


Figure 1. Location of the study area (Cabo Basin) on the southern coast of Pernambuco, Brazil.

ecosystem (Andrade-Lima, 1960; Brasil, 1972), which is practically deforested mainly for agricultural use (sugarcane), urban areas, and the port and industrial complex of Suape. Mangroves, hygrophilous fields of floodplains, and restingas occur in the vicinity (Andrade-Lima, 1960).

The selection of the area was based on the geological map (CPRM, 2005) and field evaluations, assuring the relationship of the soils with the parent material (basalt and conglomerates). In this way, three soil profiles were dug along a slope in an area without recent agricultural use (due to the scarcity of native vegetation). The P1 profile was located at the summit ($8^{\circ} 18' 46''$ S e $35^{\circ} 01' 22''$ W), the P2 profile at the half-slope position of the backslope ($8^{\circ} 18' 43''$ S e $35^{\circ} 01' 25''$ W), and the P3 profile was at the footslope ($8^{\circ} 18' 43''$ S e $35^{\circ} 01' 28''$ W), with elevations of 55, 35, and 23 m a.s.l., respectively. The declivity in the three segments was 8 % (P1), 20 % (P2), and 40 % (P3), with 140 m between P1 and P3 and 110 m between P2 and P1.

The morphological descriptions of the profiles and the sample collection were performed according to Santos et al. (2015). Collected samples were undisturbed and deformed from all horizons for physical, chemical, and mineralogical analysis. For petrographic characterization, samples of rock fragments were collected in an area close to the location of the profiles. The basalt was collected in a cut made for civil construction at a depth of approximately 5 m from the soil surface. At the base of P3, a fragment of the altered parent material was collected (conglomerates), ensuring that the base of this profile has a lithology related to the Cabo Formation (sedimentary).

Analytical procedures

Physical analyses were performed according to Donagema et al. (2011), including soil bulk density (Bd) by the volumetric ring method, soil particle density (Pd) by the volumetric flask method, and particle size distribution analysis and water-dispersed clay (WDC) by the densimeter method after slow stirring with a Wagner-type rotary shaker at 50 rpm for 16 h (Mauri et al., 2011).

Soil pH was measured in water [$\text{pH}(\text{H}_2\text{O})$] and in KCl 1 mol L^{-1} [$\text{pH}(\text{KCl})$] using a potentiometer with a soil:liquid ratio of 1:2.5 (v/v). The Ca^{2+} , Mg^{2+} , and Al^{3+} were extracted with KCl 1 mol L^{-1} , and determined using atomic absorption spectrophotometry. The K^+ , Na^+ , and available P were extracted with Mehlich-1 solution; K^+ and Na^+ were determined through flame spectrophotometry and available P through colorimetry. Potential acidity (H+Al) was extracted using 0.5 mol L^{-1} calcium acetate solution buffered at pH 7.0, and determined by titration with NaOH 0.025 mol L^{-1} . Based on the chemical analyses, we calculated the sum of base (SB), cation exchange capacity (CEC), base saturation (V), aluminum saturation (m), and activity of the clay (CECa). The total organic carbon (TOC) was determined by wet combustion, using potassium dichromate as the oxidizing agent. All chemical analyses mentioned above were performed according to the proceedings of Donagema et al. (2011).

The Si, Fe, and Al extracted by sulfuric acid digestion were determined for the upper, middle, and lower horizons of each soil profile, using the fine earth fraction according to Donagema et al. (2011). Measurements were recorded using atomic absorption spectrophotometry.

The forms of low- and high-crystalline Fe (Fed) were extracted using dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960), and low-crystalline iron (Feo) was extracted by ammonium acid oxalate (McKeague and Day, 1966). The amounts were measured through atomic absorption spectrophotometry. The Ki, Kr, Feo/Fed, and Fed/Fes ratios were calculated from the results of these analyses.

For mineralogical analyses, the organic matter in the samples was eliminated using 3 % H_2O_2 (v/v) (Jackson, 1975). The sand, silt, and clay fractions were separated after

dispersion with NaOH and slow stirring. Separation of the clay fraction was carried out by siphonation after decantation of the silt fraction and by wet sieving (coarse and fine sand). The samples of coarse sand, fine sand, and silt were analyzed by X-ray diffractometry (XRD) as non-oriented powders. The clay fraction was also analyzed as natural clay (non-oriented powder) and as oriented aggregates on glass slides after being submitted to iron oxide elimination pretreatments (Jackson, 1975).

The scanning amplitude in the powder samples was 5 to 70° 2θ, while in the samples in the form of oriented aggregates it ranged from 3 to 35° 2θ, all at the recording speed of 1° 2θ min⁻¹, using a Kα radiation of λ 0.15405 nm, produced by a copper tube, with a voltage of 40 kV and an amperage of 20 mA. The deferred clay fraction was saturated with KCl and analyzed at room temperature, 110, 300, and 550 °C (K25; K110; K300; and K550). Analysis was also performed by MgCl₂ saturation for determination at room temperature and solvated with glycerol (Mg and Mg-Gly). The samples that showed smectite minerals were subjected to the Greene-Kelly test (Greene-Kelly, 1953) by saturation with LiCl 1 mol L⁻¹, according to Lim and Jackson (1986). The criteria used to interpret the diffractograms and to identify the minerals were based on the interplanar spacing (d), according to Jackson (1975) and Brown and to Brindley (1980).

Conglomerate and basalt samples were submitted to petrographic analysis of thin sections, according to the methodology proposed by Cesero et al. (1989).

RESULTS

Morphological and physical properties

The morphological description data is presented in table 1. The soils along the slope were very deep, with a brown color with no polychromy and only subtle variations in the color of the surface horizons due to the influence of organic matter.

Table 1. Morphological properties of *Nitossolos Háplicos* (Nitisol Ferritic) on the southern coast of PE (Cabo Basin), Brazil

Horizon ⁽¹⁾	Layer	Color	Clay coating	Structure	Texture	Transition
M						
P1 - Summit - <i>Nitossolo Háplico</i> (Nitisol Ferritic)						
Ap	0.00-0.15	5YR 3/4	-	2, vf and m, sbk	very clayey	cl and fl
Bt	0.15-0.50	5YR 4/4	mod, com	2, vf and m, sbk	very clayey	dif and fl
Bw1	0.50-1.20	5YR 4/4	wea, sma	1, vf and m, sbk	very clayey	dif and fl
Bw2	1.20-2.00 ⁺	5YR 4/4	wea, sma	1, vf and m, sbk	very clayey	-
P2 - Backslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)						
A	0.00-0.14	7.5YR 3/4	-	2, vf and f, sbk	very clayey	gra and fl
BA	0.14-0.38	7.5YR 4/4	wea, com	2, f and m, abk	very clayey	dif and fl
Bt1	0.38-0.80	7.5YR 4/4	mod, com	2, vf and f, abk	very clayey	dif and fl
Bt2	0.80-1.40	7.5YR 4/4	mod, com	2, vf and f, sbk	very clayey	dif and fl
Bw	1.40-2.00 ⁺	7.5YR 4/4	wea, sma	1, vf and f, sbk	very clayey	-
P3 - Foothslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)						
Ap	0.00-0.15	7.5YR 3/3	-	2, vf and f, sbk	clayey	cl and fl
BA	0.15-0.30	7.5YR 4/4	mod, com	2, f and m, sbk and abk	clayey	cl and fl
Bt	0.30-0.63	7.5YR 4/5	mod, abu	2, vf and f, abk	very clayey	cl and fl
B/C	0.63-1.20	7.5YR 5/6	-	(m) and 1, f, sbk and abk	clayey	abr and irr
2Cr	1.20-2.00 ⁺	-	-	-	sandy clay loam	-

⁽¹⁾ Indicates weathering according to Santos et al. (2013). Abr = abrupt; abu = abundant; abk = angular blocks; cl = clear; com = common; dif = diffuse; f = fine; fl = flat; gra = gradual; irr = irregular; (m) = massive; m = medium; sbk = subangular blocks; vf = very fine; 1 = weak; 2 = moderate; - = not determined.

Profile P1 is located at the summit of the slope, presenting an A, Bn, Bw1, and Bw2 horizon sequence (w stands for weathering according to Santos et al., 2013), the hue is 5YR, with values of 3 to 4, and the chroma value is 4, differing from the other profiles by the reddish color (red bruno). Profile P2 is located at the backslope, with an A, BA, Bn1, Bn2, and Bw horizontal sequence, and profile P3 is situated at the footslope, presenting an A, BA, Bn, B/C, and Cr sequence. Both have a hue of 7.5YR, with values of 3 to 4, and a chroma value of 3 to 5 in horizons A and B (dark bruno).

The soil has a very clayey to clayey texture (Table 1); consistent with the nature of the material of origin (basalt alteration), the texture is sandy loam clay except in the Cr of P3, where there is sedimentary rock participation. The overall increase in the clay content with depth is insufficient to characterize an argic B horizon (textural ratio was less than 1.2), associated with a lack of polychromy and the clayey to very clayey texture, unlike soils from the *Argissolos* (Santos et al., 2013). The Bd values are higher in the upper horizons (Table 2). Mean Pd has approximately the same values (2.9 Mg m^{-3}) in P1 and P2 and is lower in P3.

Chemical properties

The pH(H₂O) was acidic (4.7 to 5.1), and the pH(KCl) values were approximately one unit lower than pH(H₂O), indicating a negative charge, although the CEC was low in profiles 1 and 2 (Table 3). The organic carbon content gradually decreased with depth from 20.2 to 1.7 g kg^{-1} . The exchangeable cations were dominated by Ca²⁺ and Mg²⁺, being higher in P3. Also, P3 presented a higher sum of bases (1.4 to $6.3 \text{ cmol}_c \text{ kg}^{-1}$) and a higher CEC (19.9 to $31.7 \text{ cmol}_c \text{ kg}^{-1}$) in relation to the other profiles, which had values between 2.8 and $1.0 \text{ cmol}_c \text{ kg}^{-1}$ for the sum of bases and 6.0 to $12.1 \text{ cmol}_c \text{ kg}^{-1}$ for CEC; the same behavior was observed for clay activity. The

Table 2. Physical properties of *Nitossolos Háplicos* on the southern coast of PE (Cabo Basin), Brazil

Horizon	Bd	Pd	Coarse sand	Fine sand	Silt	Clay	WDC	FD	Silt/Clay
	Mg m ⁻³		g kg ⁻¹					%	
P1 - Summit - <i>Nitossolo Háplico</i> (Nitisol Ferritic)									
Ap	1.18	2.90	37	49	291	622	100	84	0.47
Bt	1.08	2.90	24	37	242	697	0	100	0.35
Bw1	1.07	2.92	23	38	270	669	26	96	0.40
Bw2	1.01	2.94	29	39	307	624	11	98	0.49
P2 - Backslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)									
A	1.20	2.88	58	51	206	685	22	97	0.30
BA	1.05	2.90	48	45	239	667	24	96	0.36
Bt1	1.05	2.99	52	49	231	669	0	100	0.34
Bt2	1.08	2.94	62	48	176	714	25	96	0.25
Bw	1.16	2.92	53	47	196	708	0	100	0.28
P3 - Footslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)									
Ap	1.36	2.76	164	85	215	536	386	28	0.40
BA	1.19	2.70	199	103	179	519	15	97	0.34
Bt	1.17	2.74	160	95	107	639	0	100	0.17
B/C	1.19	2.72	200	107	164	529	15	97	0.31
2Cr	-	2.72	314	151	255	280	22	92	0.91

Bd = bulk density (Donagema et al., 2011); Pd = particle density (Donagema et al., 2011); WDC = water-dispersed clay, and particle size distribution determined according to (Mauri et al., 2011); FD = flocculation degree, calculated according to Donagema et al. (2011); - = not determined.

Table 3. Chemical properties of *Nitossolos Háplicos* on the southern coast of PE (Cabo Basin), Brazil

Horizon	pH		ΔpH	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al^{3+}	H+Al	SB	CEC	P	TOC	V	M
	H ₂ O	KCl													
$\text{cmol}_c \text{ kg}^{-1}$															
P1 - Summit - <i>Nitossolo Háplico</i> (Nitisol Ferritic)															
Ap	5.1	4.1	-1.0	1.4	1.2	0.10	0.13	0.3	9.3	2.8	12.1	10.8	20.2	23	10
Bt	4.7	4.0	-0.7	0.7	0.2	0.01	0.07	0.8	6.9	1.0	8.1	10.6	10.9	12	45
Bw1	4.7	4.3	-0.4	0.8	0.3	0.01	0.06	0.4	4.7	1.2	6.0	12.4	7.7	21	24
Bw2	4.7	4.1	-0.6	0.9	0.2	0.01	0.08	0.6	5.6	1.1	6.8	13.4	4.2	17	36
P2 - Backslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)															
A	5.0	4.1	-0.9	1.1	1.0	0.08	0.11	0.3	8.9	2.3	11.2	11.9	19.3	20	12
BA	4.8	4.0	-0.8	0.9	0.1	0.01	0.05	0.7	6.1	1.1	7.2	10.2	8.4	15	40
Bt1	4.8	4.0	-0.8	0.9	0.1	0.01	0.06	0.7	6.0	1.1	7.1	12.5	6.0	15	40
Bt2	4.7	4.0	-0.7	0.8	0.1	0.01	0.05	1.0	6.9	1.0	7.9	14.1	4.4	12	51
Bw	4.8	4.1	-0.7	0.9	0.2	0.01	0.05	0.8	5.6	1.2	6.8	14.7	4.5	17	41
P3 - Foothslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)															
Ap	5.1	3.6	-1.5	3.5	2.4	0.24	0.16	3.0	16.8	6.3	23.1	10.9	19.3	27	32
BA	4.9	3.4	-1.5	1.4	1.2	0.04	0.10	12.7	19.7	2.7	22.4	9.2	10.4	12	82
Bt	4.9	3.5	-1.4	1.0	0.5	0.03	0.08	10.0	19.1	1.6	20.7	9.3	10.6	8	86
B/C	4.7	3.5	-1.2	0.8	0.5	0.03	0.09	12.6	18.5	1.4	19.9	9.6	6.5	7	90
2Cr	4.8	3.4	-1.4	0.7	1.3	0.02	0.14	24.0	29.5	2.2	31.7	10.1	1.7	7	92

SB = sum of base; CEC = cation exchange capacity; TOC = total organic carbon; V (base saturation) = $100 \times \text{SB}/\text{CEC}$; m (Al^{3+} saturation) = $(\text{SB} + \text{Al})/\text{CEC}$. All chemical properties were determined and calculate according to Donagema et al. (2011).

potential acidity (H+Al) was lower in P1 and P2, ranging from 5.6 to 9.3 $\text{cmol}_c \text{ kg}^{-1}$, whereas the exchangeable acidity ranged from 0.3 to 1.0 $\text{cmol}_c \text{ kg}^{-1}$ in P1 and P2 and was very high in P3, mainly from the BA horizon, where values varied between 10.0 and 24.0 $\text{cmol}_c \text{ kg}^{-1}$. The P levels tended to increase with depth, ranging from 9.2 to 14.7 mg kg^{-1} (Table 3).

The Ki index ranged from 1.7 to 2.2 in profiles 1 and 2 (Table 4). These data agree with the mineralogical composition of the clay fraction (Table 5 and Figure 2). In spite of the smectite minerals in P3, the Ki index was 2.0 and 2.1 in the Ap and Bn horizons, respectively, and 2.7 in Cr. The increasing values of Ki with depth at P3 were correlated with increases in the intensity of diffraction peaks related to the 1.4-nm interplanar distance (smectite minerals) and the decrease in peak intensity related to the 0.7-nm interplanar distance (kaolinite) (Figure 2), indicating coherence between the Ki values and the XRD results for the clay fraction of the studied soils.

The results of selective dissolution are given in table 4. The Fed content was higher in P1 (186.0 g kg^{-1}) than in P2 (156.2 g kg^{-1}), and P3 (86.8 g kg^{-1}) at the subsurface horizon, consistent with the reddish colors (Table 1). These contents tended to increase with depth at P1 and P2, unlike P3, where the contents decreased with depth. Such values are considerably larger than the values of Feo. Thus, the soil sequence in the direction of P1 to P3 (from the summit to the foothslope) showed a reduction in Fes (Table 4), an increase in the Feo/Fed ratio (<0.05), and a reduction in the Fed/Fes (Table 4).

Mineralogical properties

Based on XRD data, quartz was the main mineral in the sand fraction (fine and coarse) in all profiles, although feldspar was also present (Table 5). Mica was observed only in the subsurface horizons of P3. In the silt fraction of all horizons, quartz, feldspar,

Table 4. Silicon, aluminum, and iron contents obtained by sulfur digestion, and Ki and Kr values, Fe contents extracted by DCB (Fed), and ammonium oxalate (Feo) and their respective relationships from the superficial, median, and lower horizons of *Nitossolos Háplicos* on the southern coast of PE (Cabo Basin), Brazil

Horizon	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Ki ⁽¹⁾	Kr ⁽²⁾	Fed	Feo	Feo/Fed	Fed/Fes	CECa
	g kg ⁻¹			g kg ⁻¹						cmol _c kg ⁻¹
P1 - Summit - <i>Nitossolo Háplico</i> (Nitisol Ferritic)										
Ap	190.0	167.4	235.5	1.93	1.02	163.63	4.57	0.03	0.70	19
Bw1	264.0	245.9	281.8	1.82	1.05	186.05	1.60	0.01	0.66	9
Bw2	216.5	217.6	307.6	1.69	0.89	181.86	1.45	0.01	0.59	11
P2 - Backslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)										
A	217.0	167.4	155.1	2.24	1.40	141.20	2.08	0.02	0.91	16
Bt1	238.0	196.3	247.3	2.06	1.14	156.21	2.01	0.01	0.63	11
Bw	223.5	255.0	198.4	1.49	0.99	140.51	1.28	0.01	0.71	10
P3 - Foothslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)										
Ap	203.5	173.4	283.8	2.00	0.97	90.65	2.05	0.02	0.32	43
Bt	238.5	193.8	187.2	2.09	1.29	80.85	1.32	0.02	0.43	32
2Cr	238.5	153.0	71.8	2.65	2.04	25.72	0.70	0.03	0.36	113

⁽¹⁾ Ki = 1.7 × SiO₂/Al₂O₃ (Vettori, 1969). ⁽²⁾ Kr = (SiO₂ × 1.7)/[Al₂O₃ + (0.64 × Fe₂O₃)] (Vettori, 1969); CECa = clay fraction activity (Donagema et al., 2011). SiO₂, Al₂O₃ and Fe₂O₃ were determined according to Donagema et al. (2011), Fed according to Mehra and Jackson (1960), and Feo according to McKeague and Day (1966).

Table 5. Qualitative mineralogical composition of the fine and coarse sand, silt, and clay (untreated) fractions of *Nitossolos Háplicos* on the southern coast of PE (Cabo Basin), Brazil

Horizon	Coarse sand	Fine sand	Silt	Clay (untreated)
P1 - Summit - <i>Nitossolo Háplico</i> (Nitisol Ferritic)				
Ap	Qz, Fd	Qz, Fd	Qz, Fd, K, Mt, Il	K, Gb, Gt, Hm
Bw1	Qz, Fd	Qz, Fd	Qz, Fd, K, Mt, Il	K, Gb, Gt, Hm
Bw2	Qz, Fd	Qz, Fd	Qz, Fd, K, Mt, Il	K, Gb, Gt, Hm
P2 - Backslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)				
A	Qz, Fd	Qz, Fd	Qz, Fd, K, Mt, Il	K, Gb, Gt, Hm
Bt1	Qz, Fd	Qz, Fd	Qz, Fd, K, Mt, Il	K, Gb, Gt, Hm
Bw	Qz, Fd	Qz, Fd	Qz, Fd, K, Mt, Il	K, Gb, Gt, Hm
P3 - Foothslope - <i>Nitossolo Háplico</i> (Nitisol Ferritic)				
Ap	Qz, Fd	Qz, Fd	Qz, Fd, K, Mt, Il	S, K, Gb, Gt, Hm
Bt	Qz, Fd, Mi	Qz, Fd, Mi	Qz, Fd, K, Mt, Il	S, K, Gb, Gt, Hm
2Cr	Qz, Fd, Mi	Qz, Fd, Mi	Qz, Fd, K, Mt	S, K, Gt, Hm

Qz = quartz; Fd = feldspars; Mi = mica; K = kaolinite; Mt = magnetite; Il = ilmenite; S = smectite; Gb = gibbsite; Gt = goethite; Hm = hematite. All analyzed according to Jackson (1975).

magnetite, and ilmenite were identified, except in the 2Cr horizon of P3 (Table 5). The constituent minerals in the clay fraction were kaolinite, goethite, hematite, and gibbsite in all profiles. Throughout P3, smectite minerals were observed, especially in the 2Cr horizon (Table 5). The Greene-Kelly test showed a complete peak expansion relative to the basal spacings of 1.0 to 1.68 nm. This behavior is attributed to smectite minerals

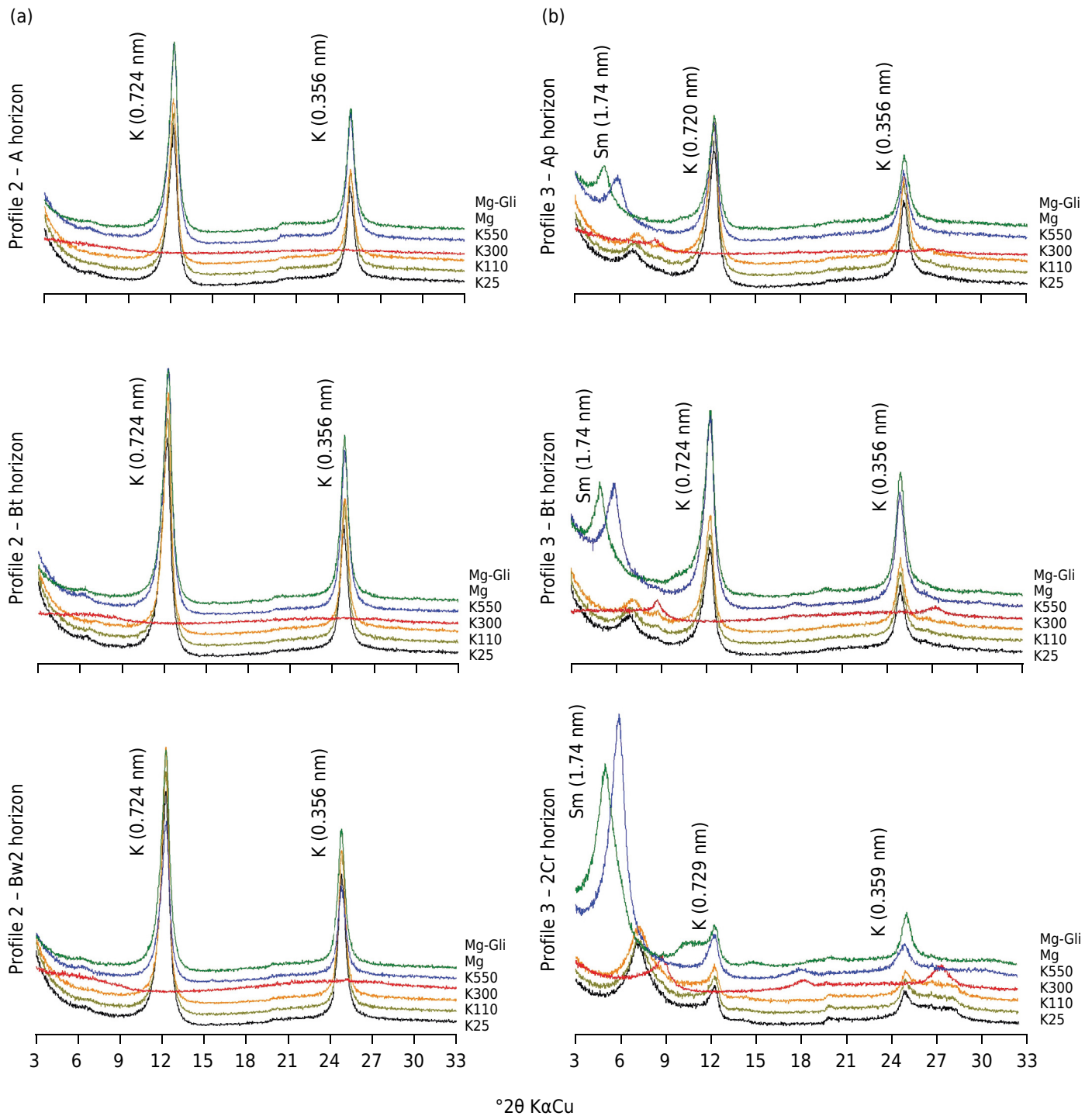


Figure 2. X-ray diffraction patterns of the treated clay fraction of the surface, median, and lower horizons. (a) P2 profile (similar to P1) and (b) P3. Sm = smectite; K = kaolinite.

with isomorphic substitution in the tetrahedral layer (Borchardt, 1989), that is, the clay fraction of P3 has beidellite and/or nontronite as smectite minerals (Figure 3), consistent with high Fe and Al values (Tables 3, 4, and 5).

Petrographic analysis

In the basalt sample, plagioclase (slat form), clinopyroxene phenocrysts (augite), sanidine phenocrysts, opaque minerals (magnetite), and zeolite filling cavities were identified, while in the conglomerate sample, although reasonably altered, microcline, orthoclase, quartz, plagioclase, biotite, muscovite, epidote, and opaque minerals were identified.

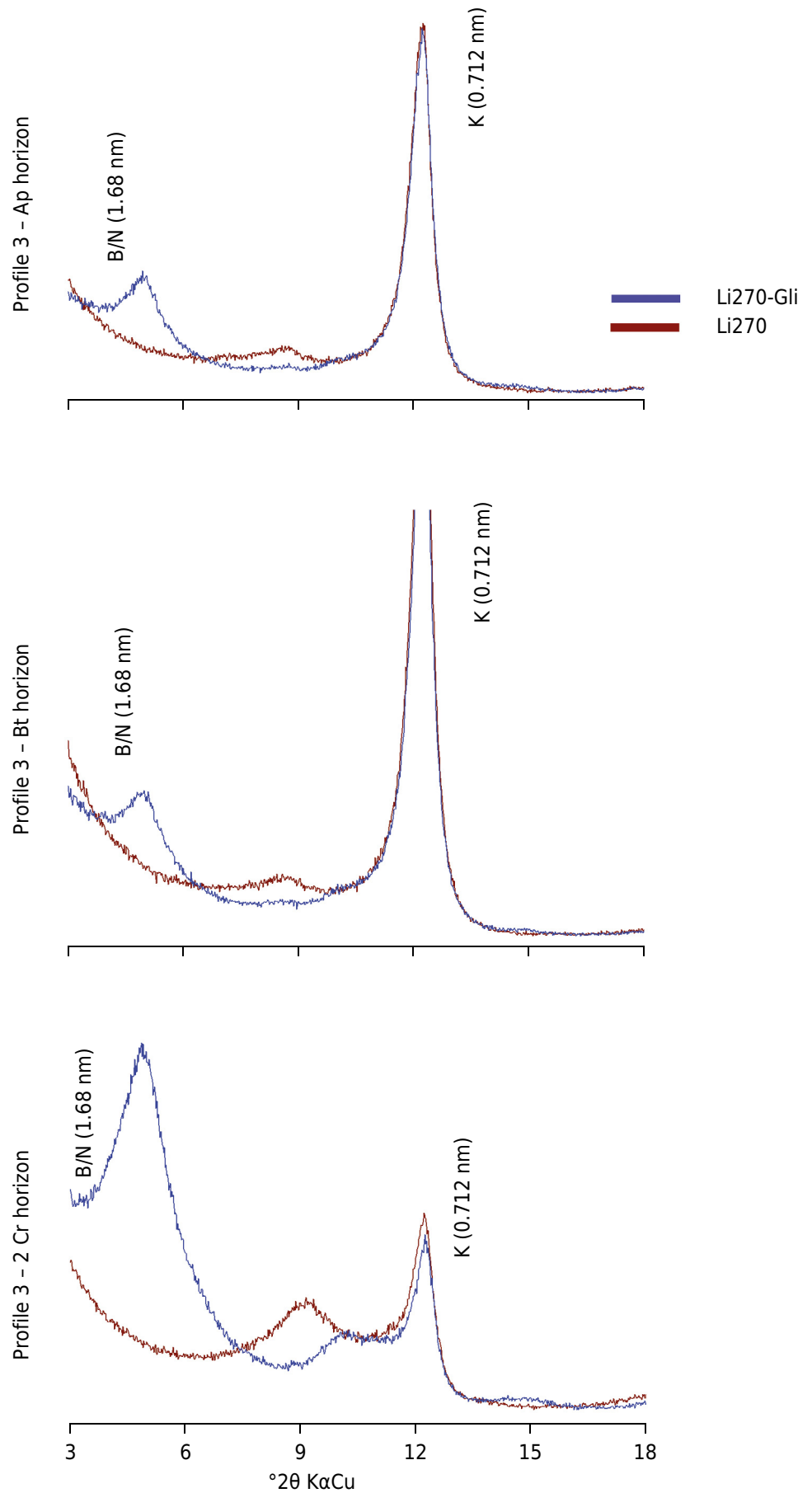


Figure 3. X-ray diffraction patterns of the clay fraction submitted to the Greene Kelly test, from the superficial, median, and lower horizons of the P3 profile. B/N = Beidelite/Nontronite; K = kaolinite.

DISCUSSION

Soil properties and their relation to pedogenesis

In general, the soils were in advanced stages of weathering, as indicated by the Ki index, the mineralogical composition, and the depth (Tables 2 and 5), in accordance with the humid tropical climate and the predominance of basic rocks (Buol et al., 1980). However, there were important differences in soil general properties according to lithology, and to a certain extent, these differences were also attributed to the slope.

Profile P1 (summit), derived from basalt, seemed to favor a greater infiltration of water compared to the other toposequence profiles due to its flat top position in the landscape, resulting in a profile with greater depth (Table 1) and Fed content (Table 4) due to the greater advance in the action of chemical weathering and due to the low loss of materials (clay) for the lower parts of the relief. Similar to P1, P2 also had a good drainage, since no redoximorphic feature was observed in field analysis, contributing to a dystrophic soil (Table 3) and the strong pedogenetic development.

Regardless of the topographic gradient, all toposequence profiles had a similar mineralogical composition in the superficial horizons, except for the presence of smectites in the fraction smaller than 2 μm , as observed in P3 (footslope). This similarity indicates material of basic origin, and an important loss of silica, as well as a loss of Fe and Al, albeit to a lesser extent, are favored by the humid climate. In addition, there was good soil drainage, even in the lowest position of the landscape. This intense weathering was confirmed by the mineralogy dominated by kaolinite and oxidic clay minerals (goethite, hematite, and gibbsite) (Table 5 and Figure 2), common in tropical soils (Schaefer et al., 2008). The soil profiles located at the highest slope positions, P1 (summit) and P2 (backslope), were subject to monosialitization, ferralitization, and alitization processes, consistent with the climate of the region and the position of the soil in the landscape (Kämpf et al., 2009). However, P3 (footslope) also presented characteristics of moderate weathering in the presence of smectite.

Soils with a nitic horizon are predominantly derived from basic to intermediate rocks (Cooper and Vidal-Torrado, 2000, 2005; Cooper et al., 2010; Santos et al., 2013; Soil Survey Staff, 2014; De Wispelaere et al., 2015), including the *Nitossolos* of the Cabo Basin (Oliveira et al., 2004; Neves et al., 2018;). In contrast to the studies mentioned and to P1 and P2 of the present study, the P3 profile (footslope), in addition to basalt, is formed from sedimentary rocks richer in SiO_2 , since the blocks and the matrix of the conglomerate package present a typical granitic composition (Alheiros and Ferreira, 1989), contributing to an unusual formation of *Nitossolo* associated with acidic and basic rocks.

The formation of *Nitossolos* under the influence of sedimentary rocks (P3) seems to have experienced pedoturbation acting in the mixture of materials (acids and basic), mainly in the more superficial horizons, which was suggested based on the reduced magnetic attraction in depth. In addition, the absence of polychromy and a textural gradient (Tables 1 and 2), despite a clear change in the parent material (product of the conglomerate change), suggests biological activity (bioturbation) (Hole, 1961; Johnson et al., 1987) in this profile. Evidence of this process was clearly observed in the other profiles of the present study, indicated by the homogeneity of the soil color and the low textural gradient along the profile, mainly in P1, where crotovins were observed (Borst, 1968). This is consistent with De Wispelaere et al. (2015), who considered biological activity important in *Nitossolos*, particularly in those developed under continued surface deposition of volcanic ash.

The smectite in P3 may be related to complex conglomerates, since they may be intercalated with argillites and shales of the Cabo Basin (Mabesoone and Alheiros, 1988; Alheiros and Ferreira, 1989). Thus, this profile of *Nitossolo* differs from those studied

by Oliveira et al. (2004) and Neves et al. (2018) for not identifying 2:1 minerals in the clay fraction.

Smectic soils that formed in a Cretaceous sedimentary environment under a tropical humid climate have also been identified by Ribeiro et al. (1990). The inference that smectite minerals are inherited from sedimentary rock is subsidized because there are no redoximorphic features indicating poor drainage under field conditions, and this could be sufficient for a current bisialitization process in these soils. Moreover, the neoformation of smectites in this environment is not excluded, although unlikely, and may constitute relics of a dry paleoclimate (Ribeiro et al., 1990; Ab'Sáber, 2000). Even under the current climatic conditions (hot and humid), there is probably still no time for total hydrolysis of these minerals.

Nitossolos commonly presents low clay fraction activity (Santos et al., 2013) as a consequence of the kaolinitic and oxidic mineralogical composition (Ferreira et al., 2003). However, the high activity identified along P3 is related to the smectites (Table 5 and Figure 2). The presence of 2:1 phyllosilicates also increased the ΔpH and CEC in P3 (Table 3) and may have contributed to the high levels of WDC in the surface horizon (Table 2), reaching high values for humid tropical soils. Smectic minerals associated with lower Fe oxyhydroxide contents reduced the Pd values in this profile (Table 2), whereas the highest Pd (above 2.8 kg dm^{-3}), observed in P1 and P2, is common in soils derived from rocks rich in ferromagnesian minerals, such as basalt (Ghidin et al., 2006).

Among the dioctahedral smectites identified by the Greene-Kelly test (Figure 3), the dominance of beidelite is more likely to be considered as an aluminous smectite mineral (Borchardt, 1989). This mineral contains the octahedral sheet consisting of Al hydroxide (Borchardt, 1989), and its geochemical destabilization can be an important source for the high exchangeable Al contents found in P3 (Table 3), as discussed in Ribeiro et al. (1990) and Cunha et al. (2014, 2015).

Profile P3 (footslope) receives material from the upper portions, but due to its undulating relief and local slope ($\approx 20\%$), this profile seems to lose more material than it receives, resulting in less depth between toposequence soils. In addition, the contribution of conglomerate material may impede weathering compared to the basic material (poorer in SiO_2), resulting in a shallower soil. The conglomerates may also explain the lower clay content in P3 (Table 2). The position of this profile in the landscape is subject to lateral water flow from the above areas, leaving it closer to the water table, resulting in moderate drainage and less leaching. Thus, it has higher Ca^{2+} , Mg^{2+} , and K^+ values in the superficial horizons due to the accumulation of material from the higher parts of the landscape (Table 3). The higher content of Mg^{2+} , in relation to Ca^{2+} , in the 2Cr horizon of P3 may be associated with biotite in the fragments of rocks that constitute the conglomerates (Mabesoone and Alheiros, 1988). Additionally, the destabilization of smectite (as discussed above) can be a source of Mg^{2+} (Kämpf et al., 2009).

Taxonomic considerations

All profiles were classified according to the criteria established by the SiBCS (Santos et al., 2013) as *Nitossolos Háplicos* and, according to the World Reference Base of Soils (WRB) (IUSS Working Group WRB, 2015), as Ferritic Nitisols. The profiles presented a dystrophic character and a high Fe content (ferric soils). In addition, P3 had an allytic character. Thus, a coherent soil classification requires a framework into new classes, related to the suborder of *Nitossolos Háplicos*. For that, it is suggested that profiles P1 and P2 are classified as *Nitossolos Háplicos distroféricos*, which is one of the classes already existing for *Nitossolos Vermelhos* and *Brunos*, while P3 is classified as *Nitossolo Háplico alitiférico*, as a suggestion to improve the third categorical level of the order of the *Nitossolos* in the SiBCS (Santos et al., 2013).

The complete classification of the profiles was performed according to the SiBCS criteria (Santos et al., 2013), in addition to the suggestions discussed above: P1 - *Nitossolo Háplico distroférico latossólico*, a moderate, very clayey texture, with subperenifolia forest phase and undulating relief; P2 - *Nitossolo Háplico distroférico latossólico*, a moderate, very clayey texture, with subperenifolia forest phase and undulating relief; P3 - *Nitossolo Háplico alitiférico típico*, a moderate, very clayey texture, with subperforfolia forest phase and undulating relief.

Relation of soil to the adjacent environment

The comparison of the studied soils with other basalt-derived *Nitossolos* (Cabo Basin) under a humid tropical climate in the south coast of PE (Nascimento et al., 2009) suggests that the processes of monosialitization and ferralitization are more active in adjacent *Nitossolos* [*Nitossolos Vermelhos* - Oliveira et al. (2004), and *Nitossolos ácidos* - Neves et al. (2018)], regardless of the position of the soil in the landscape. The lowest degree of evolution for the studied soils is indicated by the presence of easily weathered minerals (feldspars) in the sand and silt fractions of all toposequence profiles (Table 5). In addition, the occurrence of smectites in P3, which is under the influence of sedimentary rocks, increases the contrast between the *Nitossolos* studied in the present work and other *Nitossolos* of the Cabo Basin.

Other soils with Bt horizons are common in this region (Brasil, 1972) with chemical and mineralogical properties similar to those of the studied soils, such as the *Argissolos Vermelho-Amarelos* developed from the Cabo Basin rhyolites (Brilhante et al., 2017); these authors also described *Cambissolo* in this region. *Argissolos Vermelho-Amarelos* is typical of the PE coastal humid region in an area of pre-Cambrian rocks corresponding to the crystalline basement (Lima et al., 2008) and presents properties similar to those observed in the present study (mainly P1 and P2), such as base poverty, a clay fraction consisting mainly of 1:1 phyllosilicates and oxides, and being practically devoid of mineral reserves to release plant nutrients. In contrast to the studied soils (in the case of P3), the adjacent soils, including *Nitossolos* (Oliveira et al., 2004; Neves et al., 2018), present low levels of exchangeable Al^{3+} .

However, the results show that the studied soils presented properties (greater sum of bases, CEC, available P) that compare favorably with other *Nitossolos* of the Cabo Basin (Oliveira et al., 2004; Neves et al., 2018) and other soils of this basin, mainly represented by *Latossolos* and *Argissolos* (Brasil, 1972; Araújo Filho et al., 2000). This highlights the great agricultural potential of these soils surrounded by a variety of highly weathered soils, in contrast to floodplain soils such as *Gleissolos Háplicos* and *Gleissolos Tiomórficos* (Lemos, 2013), with limitations due to hydromorphic conditions.

Although quartz is present in soils of the toposequence and predominates in adjacent soils (Lima et al., 2008), especially those originated from felsic rocks (much of the Cabo Basin); the soils studied presented considerable amounts of minerals (feldspar) in the sand and silt fractions and mica in the sand fraction of P3, helping to maintain a high relative soil fertility through the release of nutrients. The occurrence of mica and smectite in *Nitossolos*, in addition to providing nutrients to plants (mainly K and Mg) by the chemical weathering of micaceous minerals, is a key factor in soil sorption properties under humid tropical conditions; such as relatively high CEC values (19.9 to 31.7 $cmol_c kg^{-1}$).

Minerals 2:1 in certain environments can contribute significantly to soil acidity, releasing high amounts of Al^{3+} (extracted by $KCl 1 mol L^{-1}$) by weathering (Cunha et al., 2014), as observed in P3 (Table 3). These minerals can be transported by erosion to associated environments (Navarre-Sitchler et al., 2011), causing damage to both natural vegetation not adapted to high levels of exchangeable Al^{3+} and to commercial crops. In associated environments, the mineralogy of the hydromorphic soils has been strongly influenced

by the geology of the basin that surrounds the coastal floodplains along the coast of PE cultivated with sugarcane (Lemos, 2013). The transport of clay by erosion can be favored by the rolling relief of the *Mares and Morros* and the high rainfall, in addition to the intensive use of the soil (Tabarelli et al., 2006).

The high levels of Fe (ferric soils) in toposequence soils indicates a high phosphate-binding capacity (Almeida et al., 2003), suggesting a high potential reserve of this nutrient. However, the low available P content can be quickly exhausted under intense agricultural activity, requiring the application of fertilizers at a high economic cost.

CONCLUSIONS

Nitossolo Háplicos (Ferritic Nitisols) in the southern coastal region of Pernambuco are formed from basalts and conglomerates, with the *solum* registering a marked influence of sedimentary material and soil topographic-hydrological conditions, presenting a high exchangeable aluminum content and the outstanding presence of smectite minerals.

The high levels of exchangeable aluminum are probably associated with the weathering of smectite minerals in addition to the possible presence of low-crystalline alumina forms.

The taxonomic classification of the studied soils requires improvement to the order of *Nitossolos Háplicos* in the SiBCS, contemplating the simultaneous occurrence of high levels of iron and aluminum, suggesting the following classes up to the third categorical level: *Nitossolo Háplico distroférico* and *Nitossolo Háplico alitiférico*.

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