Revista
Brasileira de
Ciência do Solo

Division – Soil in Space and Time | Commission – Soil Genesis and Morphology

Association of Post-Barreiras and Barreiras Formation strata and influence on soil genesis, Southern Bahia – Brazil

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ABSTRACT: The term Post-Barreiras is a definition for sediments above the deposits of the Barreiras Formation, and the genesis of soils in these environments must be related to sedimentary deposition. Our objective was to apply multi-technique analyses to characterize the sediments and soils to understand pedogenesis in these environments. We analysed sedimentological parameters and the geochronology of sediments. Morphological, chemical, and mineralogical analyses allowed the characterization of the soil. Also, these data supported the analysis of lithological discontinuity. We considered the contents of Ti and Zr, uniformity value, the fraction of organic material, morphology, and palynological analysis. The age of Post-Barreiras sediments is from the Pleistocene, and they have a more significant variation of sedimentological parameters concerning Barreiras Formation layers. In general, the soils are sandy, acidic, have a low level of exchangeable cations. Mineralogy has a predominance of quartz and kaolinite minerals. In the region, there are soils with low morphological variation, classified as Quartzipsamments. In other cases, there are soils with apparent spodic morphology, which is conditioned by four aspects: (i) Podzolization in Post-Barreiras sandy sediments without evidence of lithological discontinuity, forming Bs horizon (Spodosols); (ii) contact zones (Post-Barreiras/Barreiras Formation) with physical, chemical, and morphological evidence of discontinuity, forming Quartzipsamments or Ultisols; (iii) layers of the Barreiras Formation buried by Post-Barreiras sediments and the subsequent podzolization process, forming Bhm horizon (Spodosols); and (iv) destruction of Ultisols clay, forming Bs horizon (Spodosols). The sedimentary association (Post-Barreiras/Barreiras Formation) favors the development of different soils. The contact zones generate a morphological aspect similar to the Spodosols, associated or not with podzolization processes.

Keywords: Coastal Tablelands, lithological discontinuity, podzolization, Quaternary sediments.

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Received: March 01, 2020
Approved: June 19, 2020

How to cite: Souza CMP, Costa LM, Firmino FHT, Lima CCU, Moreau AMSS, Leite ME. Association of Post-Barreiras and Barreiras Formation strata and influence on soil genesis, Southern Bahia – Brazil. Rev Bras Cienc Solo. 2020;44:e0200015.
https://doi.org/10.36783/18069657rbcs20200015

INTRODUCTION

The Barreiras Formation are siliciclastic sediments of mostly continental origin with marine influence on sedimentation. These deposits occur on the Brazilian coast from the parallel -22° S to 04° N, sometimes forming Coastal Tablelands (Bigarella, 1975; Vilas Boas et al., 2001; Rossetti et al., 2013). Occasionally, above the Coastal Tablelands, there are discordant or concordant formations. The origin of these features varies between pedological processes forming sandy depressions (Moreau et al., 2006a; Oliveira et al., 2010; Schiavo et al., 2020). Also, by sedimentary deposition, forming the Post-Barreiras sediments (Tatumi et al., 2008; Rossetti et al., 2011; Gandini et al., 2014). In the literature, there are several pedological studies on sediments from the Barreiras Formation (Demattê et al., 1996; Moreau et al., 2006b; Cunha et al., 2019). However, studies with Post-Barreiras sediments do not focus on pedology.

Post-Barreiras sediments are geographically casual along the Brazilian coast, and it can present different granulometric characteristics due to environmental influences. In the Northern region, they are sandy deposits with structures for dissipating dunes (Tatumi et al., 2008). In the northeast region, in the Paraiba Basin, there are dune structures, and also there are hardened sandstones, mudstone, or complex types of soft-sediment deformation structures (Rossetti et al., 2011). In the state of Bahia, are sandy with dune features (Tricart and Silva, 1968), where the sands have a low degree of roundness, ranging from white and yellowish colors (Souza et al., 2016a). In general, these studies with Post-Barreiras are focused on lithostratigraphy and the origin of sediments. While pedological studies only mention Post-Barreiras sediments as parent material (Horbe and Costa, 1997).

The wind origin of the Post-Barreiras sediments in the state of Bahia (municipality of Ilhéus) is the main factor for granulometric selection of sand, generating features in the landscape similar to the *mussunungas* sandy areas (Souza et al., 2016b). However, the origin of the *mussunungas* involves the action process of acidolysis on Ultisols clay (Moreau et al., 2006a; Oliveira et al., 2010; Schiavo et al., 2020). On the other hand, the origin of Post-Barreiras is due to sedimentary deposition (Rossetti et al., 2011; Gandini et al., 2014; Souza et al., 2016a), and this aspect can influence pedogenesis.

Considering the soil as an open system, the dynamic translocation and transformation processes, can tend to mask the evidence of morphogenetic changes (Phillips and Lorz, 2008), especially in tropical environments (Cooper et al., 2002). For example, morphology with a spodic appearance, but without podzolization, is a condition influenced by the deposition of sediments (Nott et al., 1994; Anjos et al., 2013). On the other hand, podzolization can occur in allochthonous soils, generating spodic features (Waroszewski et al., 2015). Therefore, sometimes the soil morphological analysis alone is not enough (Silva et al., 2002), and recognition of geogenic heterogeneity and layer distinction requires other analyses (Waroszewski et al., 2013).

The multidisciplinary approach involves the morphological analysis of the soil, allowing the identification of the pebble line, the abrupt difference in particle-size distribution, or color between horizons unrelated from pedogenesis (Phillips, 2007; IUSS Working Group WRB, 2015). Quantitatively, the data of soil granulometric fractions allow the calculation of soil uniformity indices (Schaetzl, 1998; Ferreira et al., 2015). The fractionation of organic matter indicates the presence or absence of pedogenetic translocation processes, assisting in the identification of illuvial horizons (González-Pérez et al., 2008; Tadini et al., 2017). In the geochemical context, the Ti and Zr contents provide the idea of allochthonous or autochthonous soils (Novaes Filho et al., 2012). Furthermore, palynology geochronology allows the understanding of the geological and paleoenvironmental context of the soil (Waroszewski et al., 2015; Buso Junior et al., 2019).

Considering that the Post-Barreiras environment originates from sedimentary deposition, we believe that this process influences the genesis of soils. Our objective was to apply multi-technique analyses to characterize the sediments and soils, to understand the processes of soil genesis in the Post-Barreiras environment.

MATERIALS AND METHODS

Study area

The area of study is in the South of Bahia along the coast of the municipality of Ilhéus, between the coordinates -14° 41′ to -15° 11′ S and -39° 55′ to -38° 99′ W of Gr. The region is under the domain Atlantic Forest vegetation, with precipitation ranging from 1900 to 2200 mm annually in the coastal zone (Figure 1a).

In the coastal portion, there is the presence of Coastal Tablelands (Barreiras Formation), configured as paleocliffs, formed due to the marine progression and regression. Above the Coastal Tablelands, there is sandy material (Post-Barreiras), which is the result of deposition (Souza et al., 2016a). Sediments occur at a maximum of 5 km after the coastline, in altitudes ranging from 15 to 120 m, with a mean elevation of 60 m (Figure 1b). In the area, we collect sediment and soil samples.

Analytical procedures

We performed the dating of four Post-Barreiras sediment samples using the Optically Stimulated Luminescence (OSL) method. We use dark PVC tubes 30-cm-long and 5 cm in diameter and inserted horizontally in previously cleaned layers. They had no transparency to prevent renewed whitening by sunlight. The treatment and analysis of the samples were performed at the DATA LTDA laboratory in São Paulo, Brazil. The ages were obtained from the relationship between the Paleodose values (De) and annual dose values (Dose Rate). The OSL dating protocol was the Single Aliquot Regeneration (SAR), with 15 aliquots (grain samples). The procedures were based on Aitken (1985) and Murray and Wintle (2000).

We performed sedimentological parameters analysis in samples of Post-Barreiras and Barreiras Formation (Folk and Ward, 1957). We used 40 g samples, free of clay, silt, and organic matter, sieved in a range of 1/5 in the phi (ϕ), with sieves between -1 to 4 ϕ. From the sand weights retained in each sieve, we entered the values in the Sysgran software (Camargo, 2006). The software allows us to automatically obtain the values of median, mean, standard deviation, asymmetry, and graphical kurtosis (Folk and Ward, 1957).

We performed the morphological description on six soil profiles based on Santos et al. (2015). We collected samples of the horizons for physical, chemical, mineralogical, and palynological analysis. The collected soil was air-dried and sieved (2 mm). The soil fractions were separated into five fractions of sand using sieves, and clay and silt determined by the pipette method (Ruiz, 2005).

For chemical characterization, we used the procedures described by Teixeira et al. (2017). The pH(H_2O) and pH(KCl) were determined using a potentiometer with ratio soil:liquid equal to 1:2.5 v/v. The elements Ca^{2+}, Mg^{2+}, and Al^{3+} ($cmol_c\ dm^{-3}$) were extracted with KCl 1 mol L^{-1} solution, to determine the concentration of these three metals we use atomic absorption spectrophotometry. The contents of K^+ and Na^+ ($cmol_c\ dm^{-3}$) and available P (mg dm^{-3}) were extracted using Mehlich-1 solution. For the determination of K^+ and Na^+, the flame spectrophotometry was used, and P was based on colorimetry. For the potential acidity levels (H+Al $cmol_c\ dm^{-3}$) it was used 0.5 mol L^{-1} calcium acetate solution buffered at pH 7.0. From the chemical analyses were calculated sum of base (SB), effective cation exchange capacity (CEC_E), total cation exchange capacity (CEC_T), base saturation (V%), and Al^{3+} saturation (m%). The P in solution or remaining (mg L^{-1})

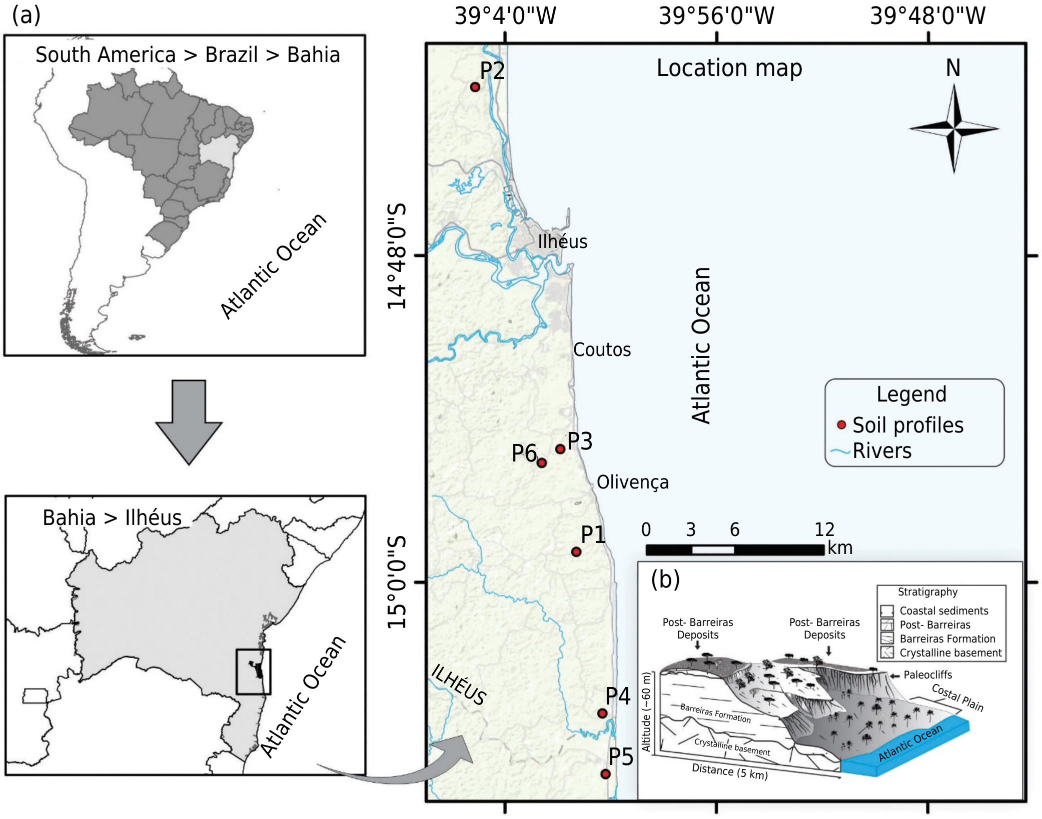

Figure 1. Location map of the study area in context: South America > Brazil > state of Bahia, with the location of the profiles in the municipality of Ilhéus (a). Block diagram illustrating the typical area of occurrence of Post-Barreiras sediments in Tablelands Costal (b).

was determined with a $CaCl_2$ solution containing 60 mg L^{-1} of P; the stirring time was 1 h, and the soil:solution ratio was 1:50.

Soil organic carbon was determined by the Walkley-Black titration method (Mebius, 1960) by wet oxidation with $K_2Cr_2O_7$ 0.167 mol L^{-1} in the presence of sulfuric acid with external heating. We fractionated the organic matter based on the differential solubility technique (Swift, 1996) with three repetitions. The fractions humin, fulvic, and humic acids were operationally determined concerning their solubilities in the aqueous environment based on the pH of the extraction solution. From organic matter fractionation data, we sought to identify if the origin of the organic sub-horizons is related to processes of illuviation.

To identify the total contents of some elements, we applied the total attack analysis by alkaline fusion (Guerra et al., 2013). We placed 100 mg of soil (sieved at 0.074 mm) and 125 mg of $LiBO_2$ below and above the soil (total 250 mg) in graphite crucibles and heated in muffle furnace up to 1000 °C for melting. For solubilization of the beads resulting from the process, we use solution HNO_3 (10 %). The contents of the elements were determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

We perform an analysis of X-ray diffraction (XRD) in some samples free of organic matter. We used PANalytical X'Pert Pro device with CoKα tube, operated between the scanning angles 4 and 50 °2θ at a scan speed of 1 °2θ min^{-1}, with a potential 40 kV generator and a current generator of 40 mA. We considered the Ti/Zr ratio for analysis of lithological discontinuity (LD) (Equation 1) (Maynard, 1992; Novaes Filho et al., 2012). We used the criterion the variability of the coefficient of variation (CV) of the relation Ti/Zr (Wilding and Drees, 1983), which show the probability of the presence of discontinuity: low (CV <15 %), moderate (CV 15-35 %) and high (CV >35 %).

We also determined the index Uniformity Value (UV), according to the Schaetzl (1998) (Equation 2), which considers the levels of total sand, very fine sand, and silt of the horizons. We used as a limit of detection of discontinuity approximate values of UV = -0.60 to 0.60, and values outside this range indicate LD (Cremeens and Mokma, 1986). The closer the LD value is to zero, the more uniform and similar are the materials of the horizons analysed (Ferreira et al., 2015).

$$\text{Relation } \frac{Ti}{Zr} = \left[\% \frac{TiO_2}{ZrO_2}\right] \times 10^2 \qquad \text{Eq. 1}$$

$$UV = \left[\frac{(S+VFS)/(TS-VFS)}{(S+VFS)/(TS-VFS)}\right] - 1 \quad \begin{array}{l} \textit{Superficial horizon} \\ \textit{Subsurface horizon} \end{array} \qquad \text{Eq. 2}$$

in which: S is silt; TS is the total sand; and VFS is the content of very fine sand.

In some organic horizons, with a total organic carbon content of more than 4 %, we performed palynological analysis. The purpose was to identify possible elements indicating whether the material was deposited or resulting from illuviation. We selected organic layers due to the possibility of being formed in a reducing environment, essential for the preservation of palynomorphs. For the palynological analysis, we perform the removal of carbonates by HCl (20 %) and dissolution of silicates by HF (70 %). Subsequently, oxidation with nitric acid (HNO_3) to palynomorph concentration, density separation of any resistant minerals, and passing through the sieve for the elimination of disseminated fine organic matter (Vidal, 1988). Samples were placed on slides and examined in detail from images captured with a Zeiss optical microscope.

We used the data set to classify soils according to the Brazilian Soil Classification System (Santos et al., 2018) and the American System (Soil Survey Staff, 2014).

RESULTS

Characteristics of sediments

In the study area, there are sandy sediments above sediments from the Barreiras Formation. They are discordant or concordant formations of white and yellowish colors (Figure 2a), sometimes with cross-stratification (Figure 2b). Geochronology indicates that they are sediments from the Pleistocene (Table 1). In general, the contact zones between Post-Barreiras and Barreiras Formation tend to be more superficial ~1.5 m, but in some cases, they are below ~6 m in depth. The contacts occur by the presence of layers with the accumulation of organic matter and/or by typical layers of the Barreiras Formation with variegated colors (Figures 2d and 2e).

The sedimentological parameters of the sediments Post-Barreiras and the Barreiras Formation (Figure 3) show that Post-Barreiras has a more significant variation in the characteristics. There is a variation of very coarse sand to fine, but with a predominance of average sand. The sands are sorted up until poorly sorted; have a prevalence of negative and very negative asymmetry; in kurtosis, most samples are platykurtic. On the other hand, the sediments of the Barreiras Formation showed more similar clusters in all parameters, with the presence of medium sand, poorly selected, negative asymmetry, and leptokurtic kurtosis.

Morphologic and physical properties of the soil

The soils have properties of the parent material and are predominantly sandy. The morphological analysis and fractionation of the soil particles are shown in table 2 and figure 4, respectively. In areas where Post-Barreiras sediments are thicker, and there are no texture changes between layers, the soils are sandy similar to the P1 profile. The

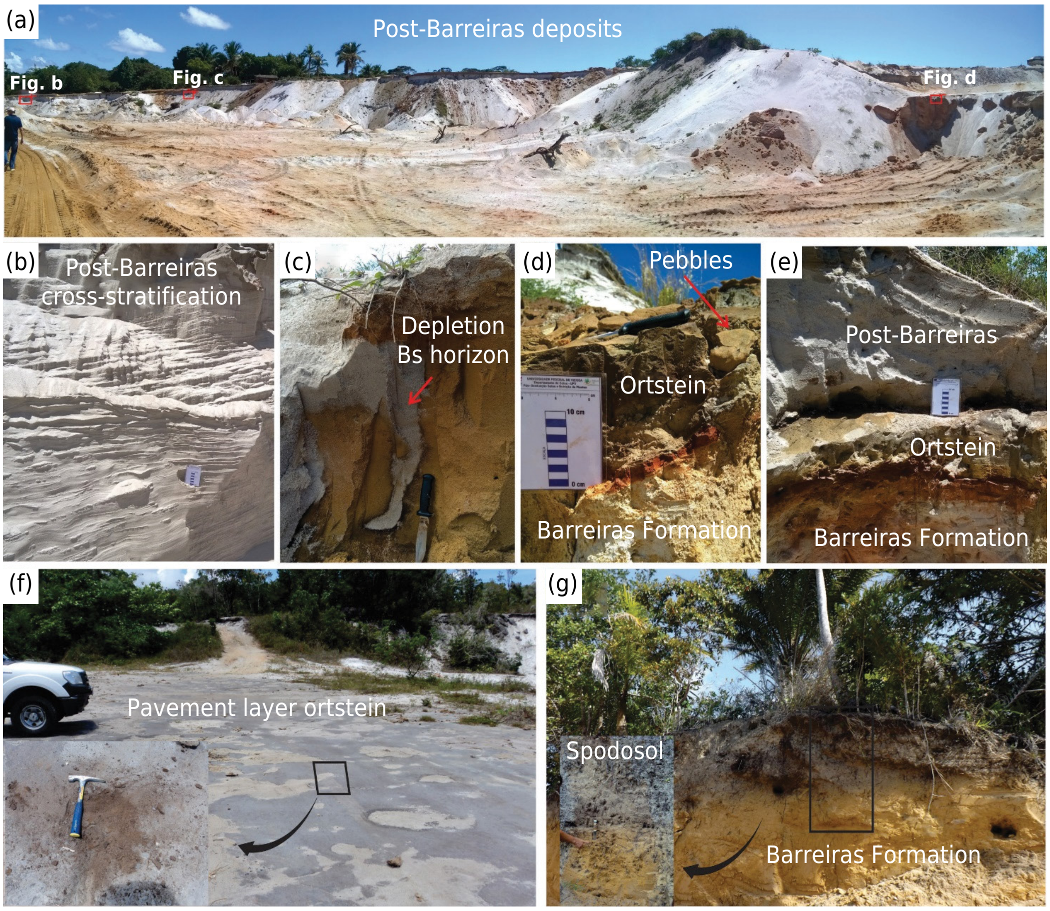

Figure 2. Typical occurrence of Post-Barreiras sediments with demarcated sedimentary and pedological features (red frame) (a); cross-stratification in Post-Barreiras sediments (b); pedological feature of organic matter and iron illuviation in Post-Barreiras sediments, with B-horizon depletion (c); contact area Post-Barreiras and Barreiras Formation, with the presence of cemented organic horizon and pebbles (d and e); residual ortstein layer after sand extraction by mining activity (f); and sandy layer resulting from pedogenesis in sediments from the Barreiras Formation, with emphasis on the Spodosol profile in these environments (g).

Table 1. Ages of the Post-Barreiras sediments obtained by optically stimulated luminescence (OSL) dating

Samples (depth)	^{232}Th	U	^{40}K	P	AD	Ages
	ppm		%	Gy	µGy yr^{-1}	ky (yr BP)
P1 (1.5 m)	2.24 ± 0.08	1.17 ± 0.37	0.36 ± 0.05	19.56	1.05 ± 150	18.750 ± 3.04
P2 (1.2 m)	2.38 ± 0.09	1.54 ± 0.08	0.36 ± 0.05	96.96	1.13 ± 80	85.350 ± 10.41
P4 (0.3 m)	2.78 ± 0.20	0.08 ± 0.10	0.45 ± 0.13	34.90	990 ± 190	35.400 ± 7.87
P6 (4.0 m)	9.99 ± 0.45	1.01 ± 0.12	1.04 ± 0.29	189.40	1.87 ± 225	101.500 ± 18.3

Radioactive isotopes ^{232}Th, ^{238}U + ^{235}U, ^{40}K; P: paleodesis equivalent dose (Gy); AD: annual dose rate (µGy yr^{-1}); ky (yr BP): years before present.

morphology indicates colors when wet from dark gray to very dark gray on A horizons and colors close to light gray on C horizons. In general, they are very friable, with a simple grain structure (Table 2).

We verified five soil profiles with apparent spodic morphology (P2 to P6). The morphology is the result of the presence of layers with yellowish colors or dark colors that occur below the sandy albic horizons. The P2 profile has an apparent spodic morphology due to the presence of a layer at a depth of 0.55 m, which differs abruptly in color (reddish yellow), concerning the upper sandy horizon, which has a light olive-gray color. In this contact zone, there is a line of rounded quartz pebbles, characteristic that is indicative of discontinuity (IUSS Working Group WRB, 2015). In the superficial layer, there are higher

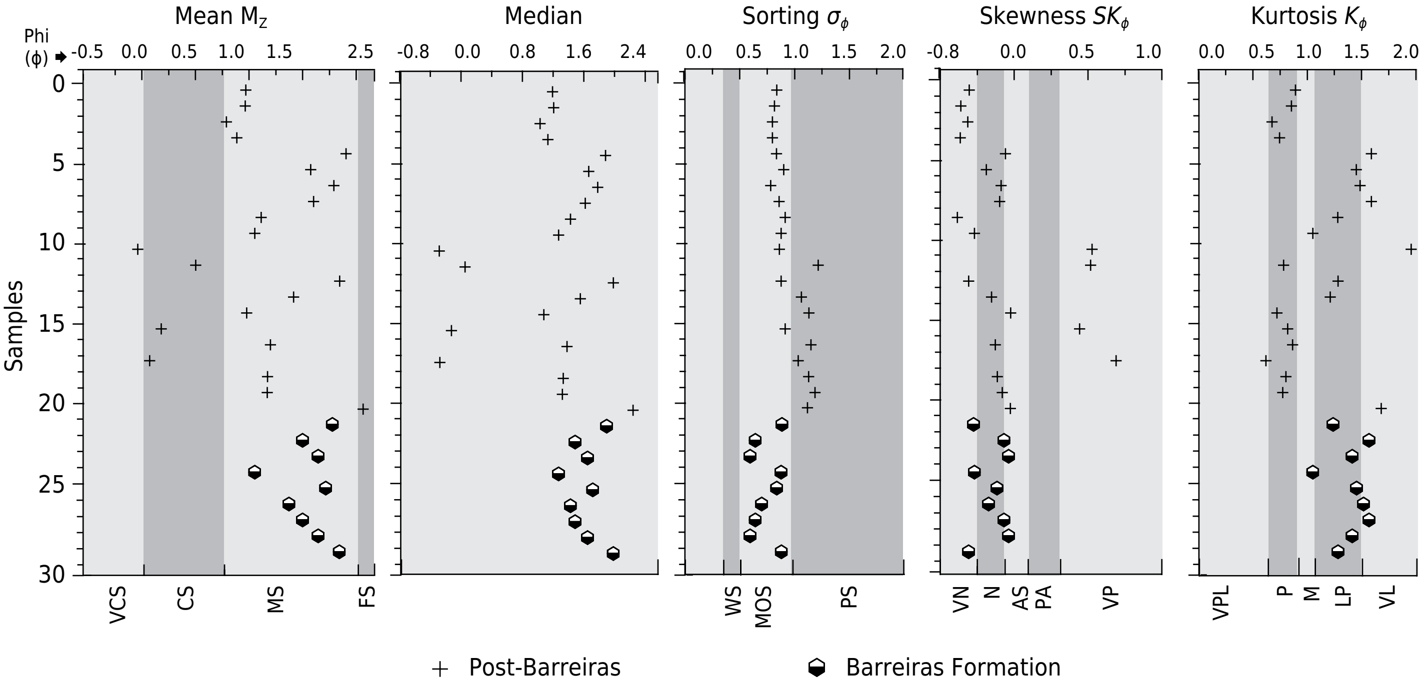

Figure 3. Sedimentological parameters of Post-Barreiras and Barreiras Formation. Mean (VCS: very coarse sand; CS: coarse sand; MS: medium sand; and FS: fine sand); Sorting σ_1 (WS: well sorted; MOS: moderately sorted; and PS: poorly sorted); Skewness (VN: very negative; N: negative; AS: approximately symmetric; PA: positive asymmetry; VP: very positive); Kurtosis (VPL: very platykurtic; P: platykurtic; M: mesokurtic; LP: leptokurtic; VL: very leptokurtic).

levels of silt, and the maintenance of this fraction may be associated with aggregation by organic matter; this implies moderate consistency when dry, while the underlying sandy horizons have weak consistency. The smallest amount of silt in the E1 horizon (0.23 to 0.49 m), indicates a probable process of illuviation. There is an increase in silt content, at a depth of 0.49 to 0.55 m, indicating that the illuviation of this fraction was recent. At depth below 0.55 m, the clay content is high.

In the P3 profile, there is a very dark gray horizon in the depth of 0.25 m, with morphology as an illuvial horizon (Bh), another possibility would be evidence of a buried A horizon. However, only with morphological analysis, it is not possible to distinguish them. Moreover, at 0.35 m depth, there is a presence of randomly rolled pebbles in the profile, positioned in a slightly hard (dry) soil matrix, with a reddish yellow color (10YR 7/6). These changes in particle size indicate LD (IUSS Working Group WRB, 2015).

The complete morphology of Spodosol occurs in P4 profile, which has homogeneous structure and consistency in all horizons, and with differentiation of colors among the horizons, characterized by the sequence A - E albic - Bs. The average sand increases in Bs horizons while reducing the fine sand fraction. The profile P5 up to the depth of 0.65 m presents similar morphology, with only color change. Below is a dark yellowish-brown color horizon and has a slightly plastic consistency. In this profile, the E horizon has darker colors and a significant presence of roots (Figure 2g).

The most significant morphological changes occur in the P6 profile. On the upper horizon, there are light colors of the sandy material. Bellow (0.67 m) it appears a horizon cemented with organic matter, of very dark brown colors, with extremely hard consistency, characterized as ortstein. In areas close to the profile, it was possible to observe that the cemented horizon can form a pavement of ortstein (Figure 2f). These are the residual structures left by the anthropic activity of sand extraction, which is common in the region. Below 0.85 m depth, there is an increase in clay content that influences the consistency of the soil, manifesting dark brown and redder colors, showing the variegated color pattern.

Table 2. Morphological properties of soils in Barreiras Formation and Post-Barreiras environments, Bahia, Brazil

Horizon	Layer	Color (Munssel)		Structure	Consistency		
		Dry	Moist		Dry	Moist	Wet
	m						
P1 - *Neossolos Quartzarênico órtico típico* (Typic Quartzipsamments)							
A	0.00-0.15	5Y 2.5/1	10YR 4/1	sg	L	Fr	NP / NST
C1	0.15-0.53	5Y 7/1	2.5Y 7/2	sg	S	Vfr	NP / NST
C2	0.53-1.30^{+}	5Y 7/1	2.5Y 7/2	sg	L	Vfr	NP / NST
P2 - *Argissolo Vermelho-Amarelo Distrófico arênico abrúptico* (Arenic Hapludults)							
A	0.00-0.23	5Y 5/2	10YR 3/1	sg	S	Fr	NP / NST
E1	0.23-0.49	5Y 6/2	2.5Y 7/2	sg	L	L	NP / NST
E2	0.49-0.55	5Y 6/2	2.5Y 7/1	sg	L	Fr	NP / NST
2Bt	0.55-1.10^{+}	5YR 6/8	2YR 5/6	mod. m. sbk	SH	Fi	SP / SST
P3 - *Neossolo Quartzarênico Órtico leptofragmentário* (Typic Quartzipsamments)							
A	0.00-0.25	10YR 6/1	10YR 5/1	sg	L	L	NP / NST
2C1	0.25-0.35	7.5YR 3/1	10YR 3/1	gr	L	Fr	LP / NST
2C2	0.35-1.50^{+}	10YR 8/4	10YR 7/6	mod. m. sbk	VH	Fi	SP / SST
P4 - *Espodossolo Ferrilúvico Órtico arênico* (Typic Haplorthods)							
A	0.00-0.10	10YR 6/1	10YR 4/1	sg	L	Fri	NP / NST
E	0.10-0.54	5Y 6/1	2.5Y 7/2	sg	L	solta	NP / NST
Bs1	0.54-1.20	10YR 5/4	10YR 4/4	sg	L	Fr	NP / NST
Bs2	1.20-2.00	10YR 5/6	10YR 4/4	sg	L	Fr	NP / NST
P5 - *Espodossolo Ferrilúvico Órtico arênico* (Ultic Haplorthods)							
A	0.00-0.10	10YR 6/1	10YR 4/1	sg	S	Fr	NP / NST
E	0.10-0.65	5Y 6/1	2.5Y 6/1	sg	S	Fr	NP / NST
Bs	0.65-1.50^{+}	10YR 5/4	10YR 3/4	md.sm.gr	S	Fi	SP / SST
P6 - *Espodossolo Ferrilúvico Órtico fragipânico* (Ultic Fragiorthods)							
A	0.00-0.19	10YR 7/1	10YR 4/1	sg	L	Vfr	NP / NST
E	0.19-0.67	10YR 3/1	2.5Y 7/2	sg	L	L	NP / NST
Bhm	0.67-0.84	10YR 4/4	7.5YR 2.5/3	st. m. sbk	VH	EF	NP / NST
Bs	0.84-0.88	10YR 5/4	7.5YR 5/3	md. m. sbk	S	Fi	SP / SST
2C1	0.88-1.04	2.5YR 5/8	2.5YR 4/6	st. m. sbk	SH	Fi	SP / SST
2C2	1.04-1.50^{+}	5YR 6/4	5YR 5/3	w. sm. gr	S	Fr	SP / SST

w: weak; mod: moderate; st: strong; sm: small; m: medium; sg: simple grains; gr: granular; sbk: subangular blocks. L: loose; S: soft; SH: slightly hard; VH: very hard; Vrf: very friable; Fr: friable; Fi: firm; EF: extremely firm; NP: non plastic; SP: slightly plastic; NST: non sticky; SST: slightly sticky.

We analysed possible lithological discontinuities (LD) by uniformity value index (UV) (Figure 4). In profiles P1 and P5, there was no indication of LD. In the other profiles, there was a variation of UV among the horizons, and UV values are out of range for uniform profiles (UV = -0.60 to 0.60). We observed that in profiles with a sandy texture, there is a variation of UV between horizons, mainly in upper horizons, for example, in profiles P2, P4, and P6, this indicates that there was a process of selection of the sand fraction during sedimentary deposition.

Chemical, mineralogical, and palynological properties of soils

In general, soils are acidic, with low pH(H_2O) and a high level of H+Al that dominates most of CEC (Table 3). In the superficial horizons, there is a tendency of a higher level of Na^+, Ca^+, and P, concerning the underlying horizons. The organic carbon content

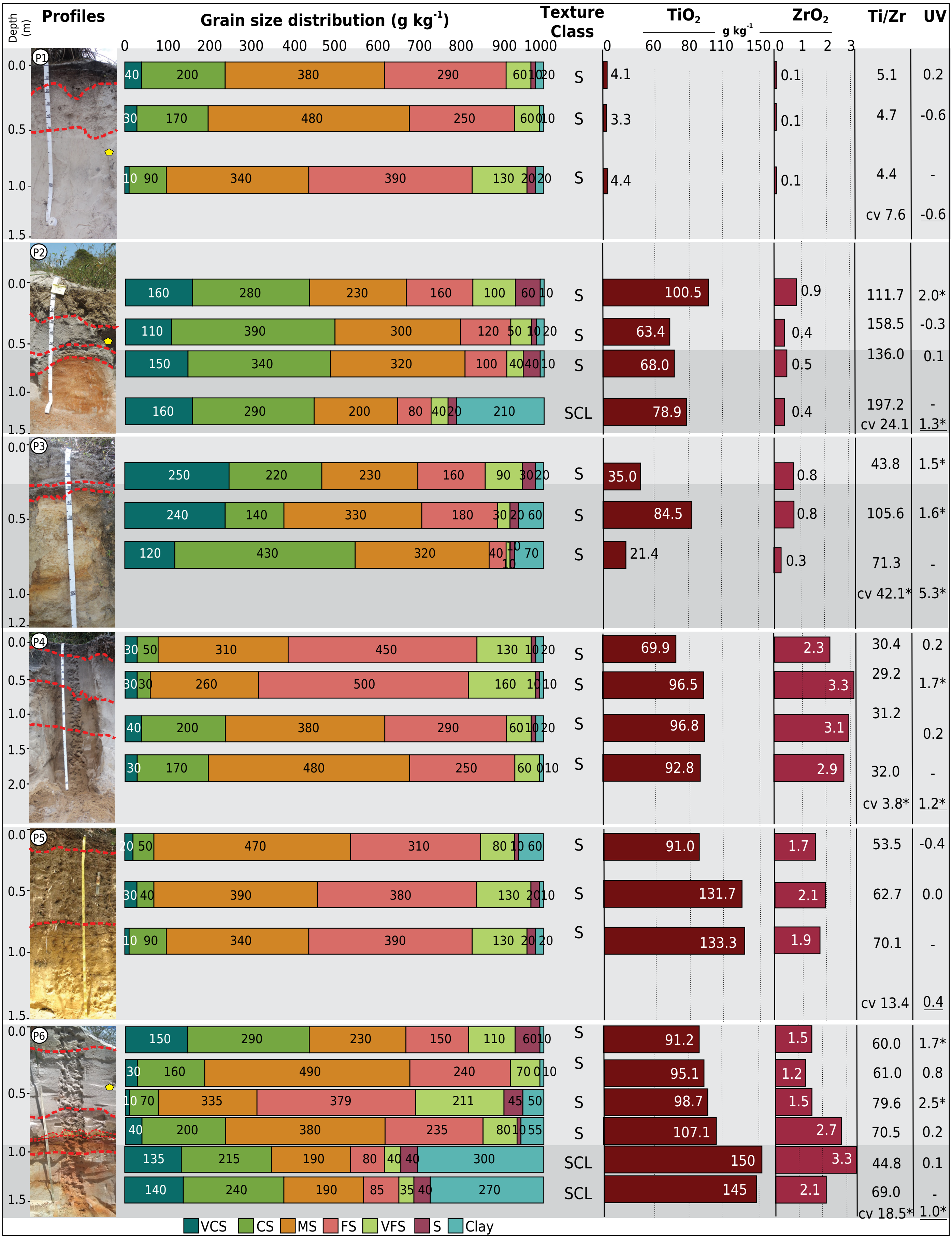

Figure 4. Distribution of particle size, texture, levels of Ti and Zr, and UV: Uniformity Value in soils developed in Post-Barreiras and Barreiras Formation sediments. Texture Class: S: Sandy; SCL: Sandy Clay Loam. * Indicative value of discontinuity and underlined UV values are calculated considering layers with morphological evidence of LD. Grain size classified as VCS: very coarse sand; CS: coarse sand; MS: medium sand; FS: fine sand; VFS: very fine sand; and S: very fine sand.

Table 3. Chemical characterization of soils in Barreiras Formation and Post-Barreiras environments, Bahia, Brazil

Profile	Hor	pH		Al^{3+}	H+Al	K^+	Na^+	Ca^{2+}	Mg^{2+}	SB	CEC_E	CEC_T	V	m	P	P-rem	OC
		H_2O	KCl														
				$cmol_c\ dm^{-3}$									%		$mg\ dm^{-3}$	$mg\ L^{-1}$	$g\ kg^{-1}$
P1	A	5.4	3.8	0.4	12.1	0.0	21.2	6.2	0.8	28.2	28.5	40.3	69.9	52.7	1.2	54.5	40.4
	C1	4.9	3.6	0.2	1.3	0.0	0.2	0.1	0.0	0.3	0.5	1.6	16.7	12.8	0.5	57.8	1.5
	C2	5.1	3.5	0.0	1.0	0.0	0.2	0.1	1.3	1.6	1.6	2.6	61.5	7.7	0.4	56.1	0.0
P2	A	5.4	4.5	0.3	2.4	1.0	2.2	0.0	0.0	3.2	3.5	5.6	57.1	39.3	2.6	43.7	2.2
	E1	6.2	4.7	0.0	0.8	0.0	0.8	0.0	0.0	0.8	0.8	1.6	50.0	50.0	0.8	57.3	0.8
	E2	6.2	4.7	0.0	1.0	0.0	0.7	0.0	0.0	0.7	0.7	1.7	41.2	41.2	0.7	52.9	0.8
	2Bt	5.5	4.0	0.1	2.2	0.0	0.6	0.0	0.1	0.7	0.8	2.9	24.1	20.7	0.6	46.3	0.8
P3	A	4.6	3.2	0.4	12.1	0.0	21.2	6.2	0.8	28.2	28.6	40.3	70.0	52.6	1.1	54.5	7.4
	2C1	5.5	4.2	0.2	1.3	0.0	0.2	0.1	0.0	0.3	0.5	1.6	16.7	12.8	0.5	57.8	25.8
	2C2	5.3	4.6	0.0	0.0	0.2	0.2	0.1	1.3	1.8	1.8	1.8	99.4	11.0	0.4	56.1	0.0
P4	A	5.0	3.6	0.3	0.2	0.0	12.2	0.4	4.3	16.9	17.2	17.1	98.9	71.3	0.9	53.6	9.6
	E	5.3	4.2	0.4	1.6	0.0	1.2	0.0	0.0	1.2	1.6	2.8	42.9	42.9	0.9	47.7	1.5
	Bs1	5.3	4.5	0.7	4.3	0.0	2.2	0.0	0.0	2.2	2.9	6.5	34.0	33.7	1.4	22.9	3.0
	Bs2	5.4	4.6	0.6	8.7	0.0	3.2	0.1	0.0	3.3	3.9	12.0	27.7	26.6	1.7	8.4	11.8
P5	A	4.2	3.0	0.3	4.0	33.0	41.2	0.4	4.0	78.6	78.9	82.6	95.2	49.9	1.3	39.2	4.4
	E	5.3	3.9	0.0	3.8	7.0	27.2	0.5	3.8	38.5	38.5	42.3	91.0	64.3	0.9	19.0	3.0
	Bs	5.1	4.2	0.0	3.3	0.0	9.2	0.8	3.3	13.3	13.3	16.6	80.1	55.5	1.7	19.0	4.7
P6	A	4.5	3.0	0.9	8.6	5.0	11.2	0.5	0.3	17.0	17.9	25.6	66.4	43.7	1.5	52.0	5.2
	E	5.0	3.6	0.3	1.1	0.0	1.2	0.0	0.0	1.2	1.5	2.3	53.0	51.3	0.7	53.6	0.8
	Bhm	4.2	3.0	3.7	13.6	5.0	12.0	0.6	0.3	17.8	21.5	31.4	56.7	38.2	1.6	59.6	46.3
	2C1	5.0	4.0	2.0	6.0	3.0	0.1	2.0	1.6	6.6	8.6	12.6	52.4	0.4	1.2	12.0	1.6
	2C2	5.6	4.1	1.2	4.0	2.0	0.0	2.5	1.5	6.0	7.1	10.0	59.9	0.2	1.0	18.0	0.9
	2C3	5.0	4.5	1.5	3.0	1.0	0.0	2.3	1.8	5.1	6.6	8.1	63.1	0.2	0.2	19.0	0.9

Hor: horizon; SB: sum of base; CEC_E: effective cation exchange capacity; CEC_T: total cation exchange capacity; V%: base saturation; m: Al^{3+} saturation; OC: total organic carbon; P-rem: phosphorus remaining (Teixeira et al., 2017).

rises in dark sub horizons; this behavior can indicate illuviation or buried horizon. For example, in the P6 profile, there is an increase of 356 % of OC between A and Bhm horizons (Table 3). In some profiles, the rise in OC is followed by an increase in P and H+Al. The P-rem levels were negatively correlated with the clay contents, and the higher clay content sub-horizons have a lower level of P-rem.

The clay fraction identified by the XRD pattern (Figure 5) was composed mainly of quartz and kaolinite. However, mineralogical differences occur in profiles with more significant morphological variation (P2, P4, and P6). In the sub-horizons of these soil profiles, kaolinite, and micas are common. Some horizons, however, present gibbsite, hematite, and goethite.

In profiles P2 to P6, the morphological characteristics indicate the possibility of LD. The profiles P2, P3, and P6 showed more considerable variation in Ti and Zr, while the other profiles showed low variation, with CV% of Ti/Zr below 13 % (Figure 4).

Considering the fractionation of organic matter (Figure 6), we observed an increase in the humin fraction in lower horizons, especially in profiles with dark sub-horizons (P3 and P6). However, the humin is not susceptible to the process of illuviation according to the pH variation (Tadini et al., 2017); therefore, this increase in humine in sub-horizons may be a consequence of the presence of LD. In profiles P4 and P5, there is an increase in soluble fractions (fulvic and humic acids), meaning the illuviation process.

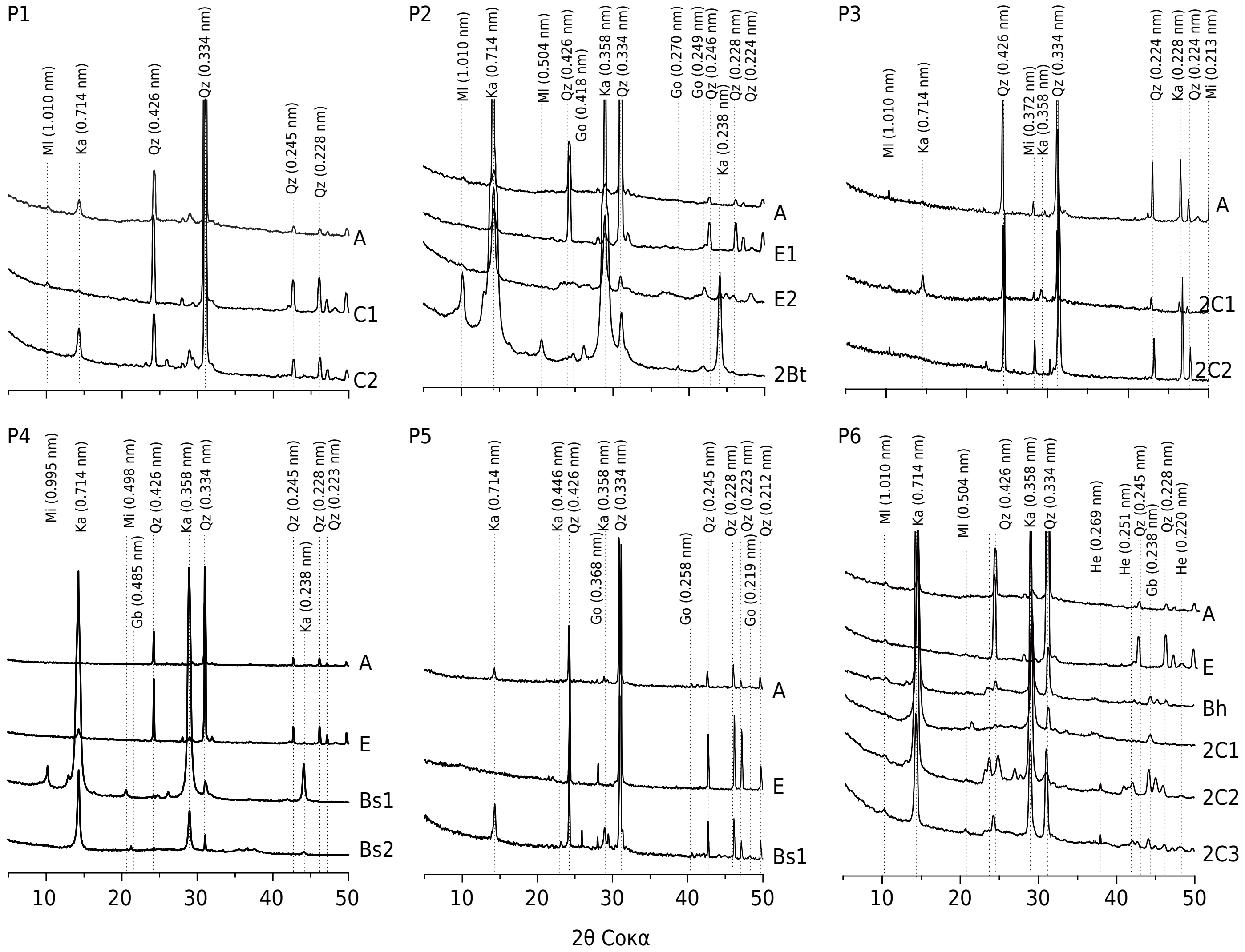

Figure 5. X-ray patterns from clay fraction (powder method) in the horizons of soil profiles. P1...P5: soil profiles. Minerals: Gb: gibbsite; Go: goethite; He: hematite; Ka: kaolinite; Mi: mica; Qz: quartz. Numbers between parentheses correspond to distance between adjacent planes in nanometers (nm).

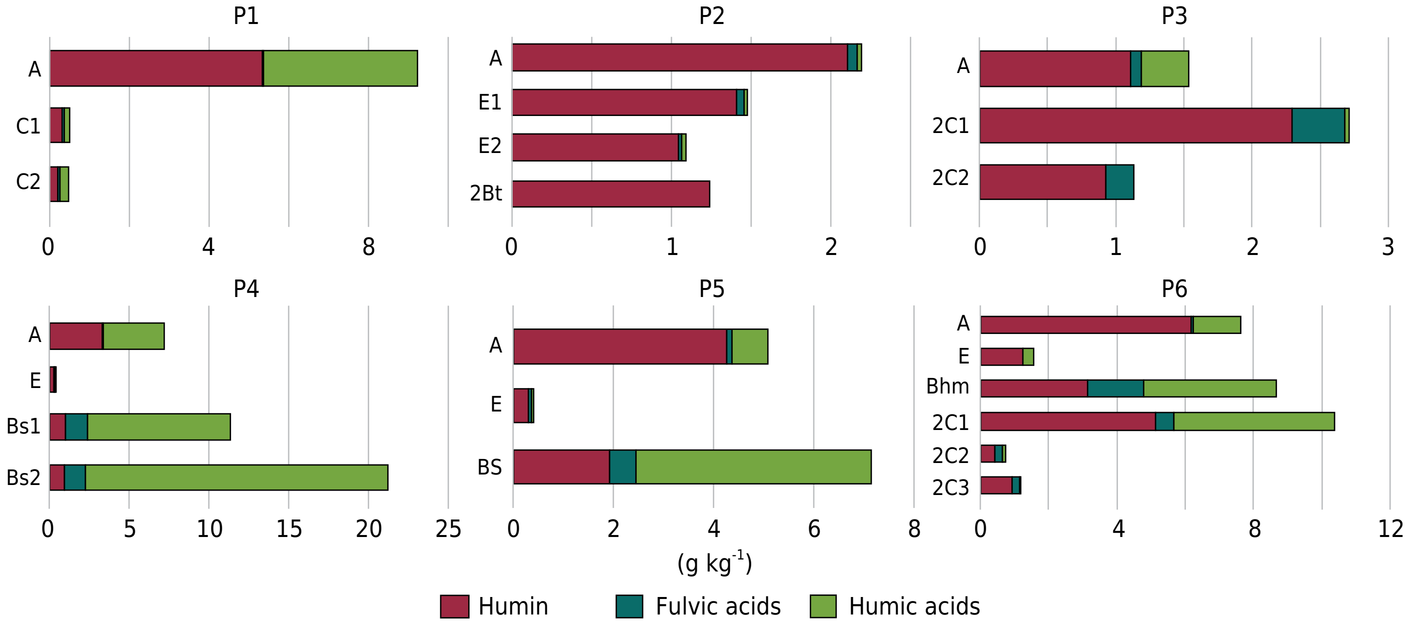

Figure 6. Fractionation of organic matter from the horizons of the collected soils.

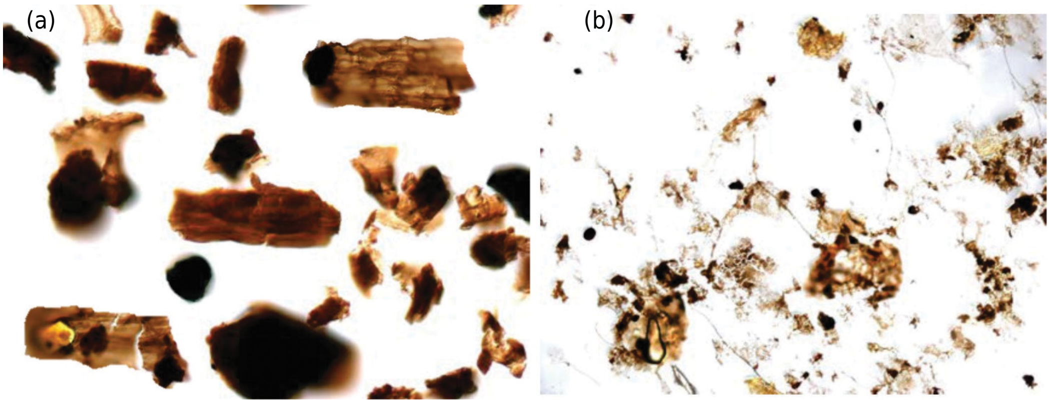

Figure 7. Vegetable cuticles, opaque phytoacetates, gelled phytoaclases present in the organic sub-horizon of the P3 and P6 profiles (a). Structures of amorphous organic matter in the organic sub-horizon (ortstein) of the P6 profile (b).

In dark sub-horizons, palynological analyses showed the presence of gelified phytoclasts derived from woody tissues (xylem) of higher plants (Tyson, 1995); these phytoclasts were more present in P3 profile (Figure 7a). However, the predominance of the amorphous organic matter suggests the presence of an illuviation process in the P6 profile (Figure 7b).

DISCUSSION

Characteristics of sediments

For some time, older studies considered Post-Barreiras sediments as a result of the weathering of the Barreiras Formation (Tatumi et al., 2008). In these environments, the intense weathering process can generate features in the landscape that are similar to stratigraphic layers. This process forms the areas of *mussunungas*, whose origin is related to the acidolysis process, creating sandy areas (Oliveira et al., 2010; Schiavo et al., 2020). However, in the study area, pedogenesis is not the main factor for the origin of the sandy regions. Since the end of the 70s, studies classified the deposits as dunes (Tricart and Silva, 1968), and this is evident by the presence of cross-stratification, typical of dune dissipation structures (Figure 2b). Furthermore, certain features allow differentiating the Post-Barreiras sediments from the *mussunungas*, as some deposits are not in depressed areas of the relief, do not have rounded shapes, and they can be up to 6 m in depth (Souza et al., 2016b).

The geochronology confirmed that sandy deposits are not associated with deposits of the underlying Barreiras Formation, whose age is Miocene to Pliocene times (Rossetti et al., 2013). Therefore, they are Post-Barreiras sediments of late Pleistocene age (Table 1), and these results are in line with other studies along the Brazilian coast (Tatumi et al., 2008; Rossetti et al., 2011; Gandini et al., 2014), including the same characteristic, which when collected in greater depth tend to be older.

The sedimentological parameters (Figure 3) in the Post-Barreiras are similar to the pattern for deposits located in northeastern Pará (Tatumi et al., 2008). However, they differ from the characteristics of the Barreiras Formation sediments; these have less variation in sedimentological parameters. The Barreiras Formation sediments showed the presence of medium sand, poorly selected, negative asymmetry, and leptokurtic kurtosis, characteristics reported in the literature (Abrahão et al., 1998; Vilas Boas et al., 2001). These distinct characteristics (Post-Barreiras and Barreiras Formation) indicate that sediments do not have a strong relationship. Furthermore, studies suggest that the sand grains of both deposits have differences in the degree of roundness, mainly in resistant minerals (zircon and tourmaline) (Ochoa et al., 2013; Souza et al., 2016b).

Soil properties and taxonomic considerations

The soils have low fertility due to the influence of pre-weathered parent material (Table 3), which has little mineralogical variation. In the upper horizons, there is a predominance of kaolinite and quartz (Figure 5). On the other hand, sandy clay sub-horizons have more crystallized kaolinite, and there is the presence of hematite, goethite, and gibbsite (P2 and P6). These minerals are common in Brazilian soils, including in Barreiras Formation environments (Moreau et al., 2006a; Cunha et al., 2019). The high regional rainfall also influences the low soil fertility because sandy soils have higher leaching (Rêgo et al., 2019)

In the upper horizons, we verified the high presence of Na^+, which is explained by the constant action of saline sprays of the coast (Magnago et al., 2013). The upper horizons show Ca^{2+}, Mg^{2+}, and mainly P concentration (Mehlich-1), this has to do with nutrient cycling (Gomes et al., 2010), favoring the increase of V% in these horizons. Furthermore, the accumulation of organic carbon (OC) in sandy soils is related to the low microbial activity (Brito et al., 2018).

In general, considering the morphological characteristics of the soil, there are two groups (Table 2 and Figure 4). The first covers profiles with little differentiation of horizons (P1), and have morphological characteristics similar to coastal plain soils (*restingas*) (Gomes et al., 2007). The second group (P2 to P6), presents substantial morphological variation between the horizons. Generally, there are layers with yellowish colors or dark colors, that occur below the sandy albic horizons, and this variation is followed by a change in texture, and subtle changes in mineralogy (Figure 5).

The Post-Barreiras sedimentation can influence the soil morphology of these environments, generating allochthonous layers. However, the high regional humidity and because they are pre-weathered sediments are factors that can hide some of the morphological criteria established by the IUSS Working Group WRB (2015) to identify discontinuity. Therefore, we consider criteria to identify possible LD to allow a better classification of the soil.

In the P1 profile, the morphology does not indicate lithological discontinuity. There is only an increase in the amount of fine sand in lower horizons (Figure 4), which may be due to wind rework during deposition, which may occur in Post-Barreiras (Tatumi et al., 2008; Souza et al., 2016a). However, this did not affect the Uniformity Value index (UV), which has a uniform behavior across horizons. Furthermore, there were no variations in the Ti and Zr contents, and the relation between both was low (Figure 4). We classify the profile as (Quartzipsamments) Typic Quartzipsamments (Soil Survey Staff, 2014), and *Neossolo Quartzarênico órtico típico* (Santos et al., 2018).

In the P2 profile, there is an apparent spodic morphology, but morphological characteristics indicate discontinuity. In morphology, there is an abrupt transition in texture and color at a depth of 0.40 to 0.55 m. In the contact zone, there is a line of rolled pebbles. Still, it is not possible to determine whether it belongs to the sandy surface layer or the clay sandy layer below, including, it may be an old superficial rocky pavement later covered by sands. However, chemical analyses of the soil matrix indicated variations of Ti, Zr, and Ti/Zr, mainly in the contact zone (Figure 4). Furthermore, the UV index showed values above the limit for uniform soils (UV = 1.3) (Schaetzl, 1998).

There is no increase in C, P, and Al^{3+} in depth (Table 3), and the levels of fulvic and humic acids are negligible in the sandy clay loam horizon (Figure 6). This behavior does not correspond to the pedogenesis of Spodosols because podzolization is necessary (Oliveira et al., 2010; Martinez et al., 2018; Menezes et al., 2018). However, there is an increase in silt content in E2; this intensity for migration of silt is a possible indication for movement also of clays. Despite the lower clay content in E2 compared to E1, in the absence of micromorphological data, the hypothesis raised is that the drainage restriction in the clay-rich horizon may favor the destruction of clay (ferrolysis). Therefore, the increase in clay in the last layer does not result exclusively from discontinuity and fits the SiBCS criteria for the Bt horizon (Santos et al., 2018). We classify the profile as (Ultisols) Arenic Hapludults (Soil Survey Staff, 2014), and *Argissolo Vermelho-Amarelo Distrófico arênico abrúptico* (Santos et al., 2018).

Morphology with a spodic appearance occurs in the P3 profile by the accumulation of organic matter in the depth of 0.35 m. However, there are rounded pebbles below the darker sub-horizon (Figure 4). These significant changes in particle size distribution suggest LD (IUSS Working Group WRB, 2015). Quantitatively, there were substantial variations in the UV index; between the first and last layer, the value was UV = 5.3, also indicating LD.

There was variation in the levels of Ti and Ti/Zr (CV = 42.1 %). These elements have low mobility since the source of these elements is resistant minerals. Furthermore, the concentration of these elements in soils of the Barreiras Formation, tend to be relatively uniform in the profile, the variations occur according to the position of the soil profile in the landscape (Bravard and Righi, 1989; Carvalho et al., 2013a). Therefore, the chemical factor also denotes LD.

Still in P3 profile, in the dark-colored sub-horizon, there was a higher content of humin (Figure 6), but, in spodic horizons, there must be a more significant amount of humic and fulvic acids, since these have solubility dependent on pH (Tadini et al., 2017). The presence of gelified phytoclasts derived from woody tissues (xylem) of higher plants (Figure 7a), explains the high content of humin in the organic sub-horizon. On the other hand, amorphous organic matter, which is a component of podzolization by dissolved organic matter (Buurman and Vidal-Torrado, 2015; Lopes-Mazzetto et al., 2018), is not predominant in the sub-horizon. Therefore, considering the physical and chemical indications of LD, and the more significant presence of humin in the organic sub-horizon, the probability of being an A horizon buried gains strength. Based on these considerations, we classify the profile as (Quartzipsamments) Typic Quartzipsamments (Soil Survey Staff, 2014) and *Neossolo Quartzarênico Órtico típico* (Santos et al., 2018).

In the P4 profile, there is a variation in the UV index between E and Bs1 horizons (UV = 1.7). Still, this granulometric behavior must be related to the process of selecting fine sands on the surface by the wind, and the Post-Barreiras sediments in the region have the aeolian origin (Tricart and Silva, 1968; Souza et al., 2016a). However, the values of Ti, Zr, and Ti/Zr tended to be uniform (Figure 4), and do not indicate LD. Another factor is a reduction of low-mobility organic fractions in lower horizons. At the same time, humic and fulvic acids increase, and the same behavior occurs for OC (organic carbon) and P. These characteristics are indicative of the podzolization process in the genesis of Spodosols (Buurman and Jongmans, 2005; Oliveira et al., 2010; Schiavo et al., 2020). Furthermore, in some areas close to the profile, there are features of depletion of the Bh horizon (Figure 2c), and this feature is the result of increased drainage in the Spodosols profile (Lopes-Mazzetto et al., 2018). We classify the profile as (Spodosol) Typic Haplorthods (Soil Survey Staff, 2014), and *Espodossolo Ferrilúvico Órtico arênico* (Santos et al., 2018).

In profile 5, the low value of UV index (UV = 0.4), and moderate variation of Ti/Zr (CV = 13.4 %), indicate that the profile has lithological uniformity (Figure 4). However, there is an increase in the clay content below 0.65 m, without criteria for textural gradient (Santos et al., 2018), and others studies have identified the same behavior in Spodosols of Coastal Tablelands (Oliveira et al., 2010; Carvalho et al., 2013b). Moreover, there is an increase of OC and P in the Bs horizon concerning the E horizon (Table 3), and the fractionation of organic matter indicated selective translocation due to the higher content of fulvic and humic acids in the subsurface (Figure 6). Therefore, the combination of these processes shows podzolization (González-Pérez et al., 2008; Oliveira et al., 2010; Tadini et al., 2017).

We attribute the evolution of the P5 profile in a similar way to the Spodosols of *mussunungas* areas (Moreau et al., 2006a; Oliveira et al., 2010). Therefore, the main factors are the destruction of clay by acidolysis, and subsequent migration of humic and fulvic acids. Five factors support this argument: (i) the region has high precipitation (1900 to 2200 mm); (ii) the source material is sediments from the Barreiras Formation; (iii) the sandy surface layer has a lot of root activity, a feature not common in Post-Barreiras in the region (Figure 4); (iv) there was no evidence of lithological discontinuity; and (v) the profile there is a podzolization process. We classify the profile as (Spodosols) Ultic Haplorthods (Soil Survey Staff, 2014) and *Espodossolo Ferrilúvico Órtico arênico* (Santos et al., 2018).

In the P6 profile, the configuration is Post-Barreiras sediments above the Barreiras Formation. This pattern generates a moderate variation in the Ti/Zr ratio (CV = 18.5 %), the UV index was 2.5 in the contact area, and UV = 1.0, between the first and last layer (Figure 4). However, podzolization in the profile is evident by the presence of a cemented sub-horizon with a high content of OC (Table 3), and the has characteristics of ortstein (Figure 2e). Metallic compounds, especially Al levels, influence the degree of cementation (Oliveira et al., 2010; Gomes et al., 2017), and that element is high on the horizon (Table 3).

The fractionation of organic matter in the P6 profile indicated a high content of fulvic and humic acids in the subsurface (Figure 6). Simultaneously, the more significant presence of organic matter in the amorphous horizon ortstein (Figure 7b). Both characteristics indicate podzolization (Silva et al., 2019; Schiavo et al., 2020). However, in the contact zone between the Bhm and 2C1 horizons, the humin content is high (Figure 6). Presumably, there is a simultaneous presence of a buried A horizon, and the podzolization process was strong enough to overcome the old morphological characteristics of A horizon. Similarly, other studies have identified this behavior in the pedogenesis of Spodosols (Dalsgaard and Vad Odgaard, 2001; Waroszewski et al., 2013, 2015).

The Bhm horizon of the P6 profile is formed in the contact zone (Pos-Barreiras/Barreiras Formation), and studies indicate that the difference in porosity between soil layers influences the origin of spodic horizons (Coelho et al., 2012; Gomes et al., 2017). Therefore, in the profile, the Barreiras Formation hinders the infiltration of water, and consequently, the illuviation of dissolved organic matter, favoring the formation of the Bhm spodic horizon (Figure 2e). We classify the profile as (Spodosols) Ultic Fragiorthods (Soil Survey Staff, 2014), and *Espodossolo Ferrilúvico Órtico fragipânico* (Santos et al., 2018).

In general, in the study area, there are different factors to generate a spodic appearance or form real spodic horizons: (i) the Post-Barreiras sedimentation above the Barreiras Formation generates an apparent spodic feature (P2 and P3). However, there is chemical, physical, and morphological evidence of LD. Moreover, there is no podzolization, and this characteristic is reported by Anjos et al. (2013); (ii) podzolization, a typical process for the formation of genuine spodic horizons (Buurman and Jongmans, 2005; Martinez et al., 2018), in the case of the P4 profile, forming Bs horizons; (iii) acidolysis process leading to degradation of Ultisols clay from Barreiras Formation (P5 profile). This behavior occurs similarly in Coastal Tablelands (Moreau et al., 2006a; Oliveira et al., 2010; Schiavo et al., 2020); and (iv) co-association of the deposition process and podzolization (P6 profile), because of the existence of Post-Barreiras above the Barreiras Formation, being a similar phenomenon in other studies (Dalsgaard and Vad Odgaard, 2001; Waroszewski et al., 2013, 2015).

In general, our results demonstrate that podzolization processes can occur in uniform profiles or with LD. The sandy matrix of Post-Barreiras sediments facilitates this process. Therefore, although some profiles do not fit the criteria for Spodosol (P2 and P3), the podzolization process is possible. However, these findings were only possible by applying a multi-technical approach. Therefore, this indicates the need for adaptation of Brazilian Soil Classification System (Santos et al., 2018) in terms of more concise delimitations of the attributes for defining spodic horizons.

CONCLUSIONS

In the study area, the Post-Barreiras sediments are sandy deposits of late Pleistocene time, and present a more significant variation in sedimentological parameters compared to sediments from the Barreiras Formation. The pre-weathered parent material, predominantly quartz and kaolinite minerals, contribute to soils with low fertility.

Quartzipsamments are present in thick Post-Barreiras sedimentary deposits. In this environment, it also supports podzolization allowing the pedogenesis of Spodosols.

In contact zones (Post-Barreiras/Barreiras Formation) generate characteristics with spodic appearance morphology but without podzolization. However, there are soils with this lithological discontinuity co-associated with podzolization, forming Spodosols.

The Acidolysis process in sediments from the Barreiras Formation allows the pedogenesis of Spodosols.

ACKNOWLEDGMENTS

We thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for providing a doctoral scholarship to the first author. The Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), process number: 88882.315083/2019-01. The State University of Santa Cruz (UESC) and friends Alan Azevedo, Glauber Guirra, Hogana Póvoas, and Liliane Góes that helped in the logistics in the fieldworks. We thank Luiz Aníbal for his help in classifying the soils.

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