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Chemical and mineralogical constitution of redoximorphic features and mechanism of formation of Plinthosols from the Araguaia River plain, Brazil

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ABSTRACT: Currently in Brazil, large grain cultivation projects on Plinthosols are a reality, however, there is little or no knowledge of the real mechanism of formation of the plinthite feature, in addition to what is reported in the literature as being a product of oxidation-reduction processes of iron element. This study evaluates iron redoximorphic features and investigates their chemical and mineralogical composition in two profiles of Plinthosols from the Araguaia River plain (P1 and P2). The study strengthens the understanding of the pedogenetic processes involved in the formation of mottles and plinthite. In this sense, it assesses whether the formation mechanisms corroborate the literature. Soil features were sampled in the upper right and left position at the initial plinthic horizon, upper right and left position at the main plinthic horizon, and lower right position at the base horizon of the plinthite zone in the profile. Separated samples comprising the soil matrix, mottles, and plinthite under natural moisture conditions were ground into powder form for chemical determinations by X-ray fluorescence (XRF), sulfuric acid attack (H_2SO_4), sodium dithionite-citrate-bicarbonate (DCB), and ammonium acid oxalate; and mineralogical determinations by X-ray diffraction. Iron contents in all determined forms were always higher in the plinthite feature, intermediate in the mottle feature, and lower in the soil matrix feature. Most of the Fe in all redoximorphic features is included in the structure of primary minerals and their derivatives (vermiculite, illite, and VHEs). Only part of the iron present (about 35.40 % in P1 and 41.98 % in P2) is detected in the form of oxides such as goethite and hematite, which could be formed in redox processes. The mottle and plinthite features under study are not the product of the classic process of segregation, mobilization, and accumulation of iron as a consequence of redox processes. These features were formed or emerged as a result of a relatively slow and constant weathering process of their source material, which is gradually decomposed in an aqueous medium, releasing most of its components. These components include iron and more mobile elements such as bases and silicon, which leave the system through drainage water, and of which a small part may eventually recombine to form new less complex minerals such as kaolinite and oxides.

Keywords: alluvium-colluvial, plinthite formation, goethite, hematite, mica, redox process.

INTRODUCTION

Soil redoximorphic features present morphological aspects expressed by distinct colors, which take place in soils from humid environments or with variations in moisture, in current or past conditions. These aspects usually relate to losses (depletion areas) or gains (accumulation areas) of pigmenting agents (Schoeneberger et al., 2012; Vepraskas et al., 1994; Zhao et al., 2019). Among the most common and certainly the most important redoximorphic features occurring in Brazilian soils is plinthite (Soil Survey Staff, 2014; Santos et al., 2018). In addition to defining a diagnostic horizon (plinthic horizon), it is also a diagnostic attribute for soil class identification (*Plintossolos*) in the Brazilian Soil Classification System “SiBCS”(Santos et al., 2018).

Significant areas with soils that present plinthite are frequent in several regions of Brazil (Anjos et al., 1995; Coringa et al., 2012; Garcia et al., 2013; Martins et al., 2018a). According to estimates, Plinthosols occupy an area greater than 589 thousand km^2 in the national territory, which corresponds to approximately 7 % of Brazilian soils (Santos et al., 2011). Among the main areas in which these ferruginous features occur in the country, the Amazon region (Alto Amazonas, Amapá State, and Ilha de Marajó), Pantanal Mato-Grossense, Ilha do Bananal, Baixada Maranhense, northern Piauí, southwestern Tocantins, and Northern Goiás (Santos et al., 2018; IUSS Working Group WRB, 2022).

Despite the importance of this soil class, few studies evaluated the genesis and morphology of Brazilian Plinthosols (Anjos et al., 1995; Coelho and Vidal-Torrado, 2003; Martins et al., 2018b). The extensive use of these soils (mainly haplic and argiluvic soils) in large agricultural projects in irrigation and drainage systems has determined the direction of research to better understand their formation processes or mechanisms, as well as characteristics that define their pattern in the face of different usage demands.

According to the specialized literature (Daniels et al., 1978; Soil Survey Staff, 1999, 2014; Eze et al., 2014; IBGE, 2015; Santos et al., 2018), plinthite (term derived from laterite, originally defined in a study by Buchanan in 1807) is a redoximorphic feature consisting of a mixture of clay, rich in iron (Fe) or iron and aluminum (Al), poor in organic carbon, with grains of quartz and other minerals, that can be morphologically observed in the form of red, yellowish-red, and dark-red mottles. According to Coringa et al. (2012), Tardy (1993) and Van Bodegom et al. (2003), plinthite genesis occurs in a humid environment by Fe segregation. This process comprises the steps of mobilization, transport, and final concentration of Fe compounds. Anjos et al. (2007), Daniels et al. (1978), Gray and Murphy (1999) and Osher and Buol (1998) observed that these features occur in poorly drained places, in the lower third of slopes, and floodplains.

Alexander and Cady (1962) mentioned plinthite has a wide range of chemical characteristics, while Roquin et al. (1990) considered this material correlates with the degree of evolution and nature of its source material. However, these authors state the most abundant elements in this redoximorphic feature are usually silicon (Si), aluminum (Al), and iron (Fe), although other elements may occur in smaller proportions.

Studies by Martins et al. (2018a,b) on the same soil profiles of this study showed total chemistry data by X-ray fluorescence (XRF) and by sulfuric acid attack in samples of matrix and plinthite features. In the same context, Maranhão (2018) detected in soil samples air-dried about 15 g kg^{-1} Fe extracted by dithionite-citrate-bicarbonate (Fed) and about 0.8 g kg^{-1} Fe extracted by ammonium acid oxalate (Feo) in the main plinthic horizon of the Plinthosols of the Araguaia River plain. By using XRD, Moura (2015) identified the following materials in the clay and silt fractions of soil profile P1: kaolinite, illite, vermiculite with Al hydroxide in the interlayer (VHE), and gibbsite, with quartz being the main mineral present in the silt fraction. In this same study, the authors also identified feldspars and micas in the silt fraction, and considered these minerals to be inherited from the source material. In turn, goethite and hematite were the most common crystalline Fe oxides in the composition of plinthites.

Plinthite composition chemically differs from soil matrix composition due to the greater amount of Fe oxides in the first (Gallaher et al., 1974; Singh and Gilkes, 1996). Based on the above, the main hypotheses of this study are: i) redoximorphic features are mainly influenced by the variation in the redox states of the iron element, which is the most active element; ii) iron, oxides and hydroxides are the main responsible for the composition and formation of plinthite.

The present study determines the chemical and mineralogical composition of redoximorphic features and evaluates the iron element present in these features in profiles of Plinthosols from the Araguaia River plain. The study intends to clarify the pedogenetic processes and the mechanisms involved in the formation and hardening of mottles and plinthite, particularly plinthite. Finally, it may confirm or not the formation mechanisms suggested in the available literature.

MATERIALS AND METHODS

Study area location

The study was carried out using two Plinthosols profiles from the Araguaia River plain, in the district of Luiz Alves, São Miguel do Araguaia city, Goiás State, Brazil (Figure 1). Geographic coordinates are as follows: 13° 14’ 38.17” S, 50° 33’ 16.97” W, altitude of 218 m (profile P1); and 13° 12’ 17.75” S, 50° 31’ 28.61” W, altitude of 216 m (profile P2). Climate in the region is Aw tropical with a dry winter season (Köppen classification system), with average annual rainfall between 1800 and 2000 mm and average annual temperature ranging from 25 to 26 °C (Cardoso et al., 2014). Two soil profiles under study were routinely characterized in the study by Martins et al. (2018a) and classified both as *Plintossolos Argilúvicos Distróficos típicos*, according to norms specified in Santos et al. (2018), and as Stagnic Plinthosol (Clayic, Orthodystric, Humic, Vetic), according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2022). Routine analytical characterization was performed by Martins et al. (2018a), who used the standard methods adopted by Embrapa (Teixeira et al, 2017).

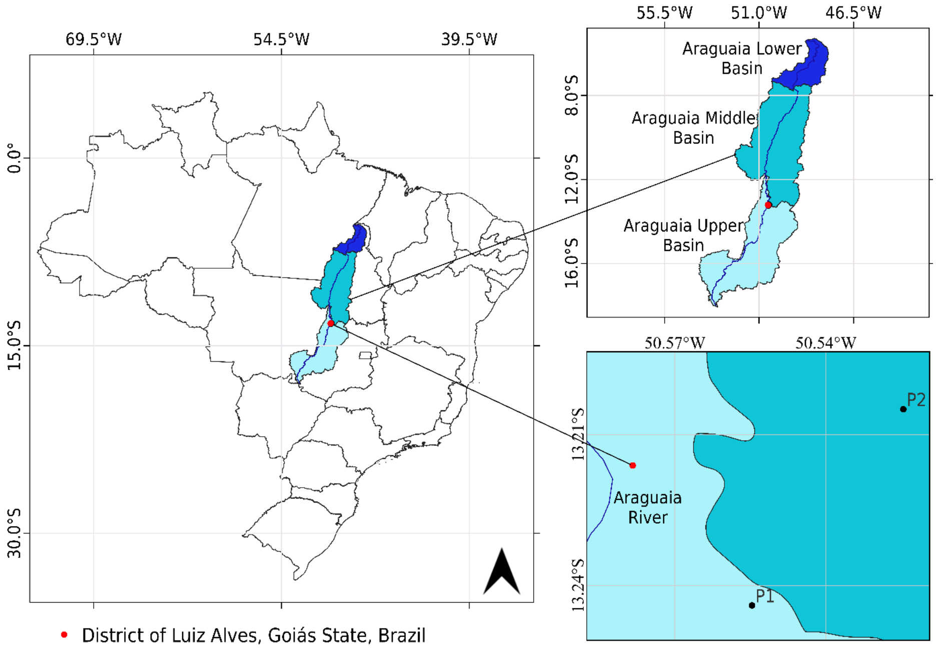

Figure 1. Location of soil profiles in the Araguaia River floodplain.

Profile P1 occurs in the Araguaia hydrographic basin, in the upper Araguaia segment, in an area of the Cenozoic Coverage eological province, in the Bananal unit, geomorphological domain of Quaternary Sedimentary Deposits. However, profile P2 occurs in the middle Araguaia segment of the same hydrographic basin and also takes place in an area of the Cenozoic Coverage province, in the Bananal unit, in Quaternary Sedimentary Deposits (RadamBrasil, 1981; ANA, 2016; IBGE, 2021).

The region presents a flat relief with the presence of murundus under natural vegetation of Campo Cerrado (Brazilian Savanna) in a situation of seasonal variation of the water table. Murundus are rounded-shaped elevations on the surface of the land, with different origins. They have dimensions that can reach 20 m in diameter and 2 m in height (IBGE, 2015). Soils remain naturally submerged in the rainy season and with a water table at medium depths in the dry season (>1.80 m from the surface). In addition to the natural fluctuation of the water table due to the alternation of rainy and dry seasons, exploration activities employing flood irrigation in annual crops in the vicinity, by the Luiz Alves Irrigation Project, interfere with the natural dynamics of the floodplain.

We collected samples of redoximorphic features in the initial or upper plinthic horizons, the main plinthic horizon, and the base or lower plinthic horizon (Figure 2). From each position (Pst) sampled, the redoximorphic features present were separated for the necessary determinations. Both profiles have alluvial-colluvial sediments as their source material, belonging to the Phanerozoic Cenozoic Quaternary Pleistocene Gelasian, of the Bananal sedimentary cover (RadamBrasil, 1981; Martins et al., 2018a,b; Santos et al., 2022).

Sampling and preparation of redoximorphic features for analysis

Different positions for sampling the soil matrix, mottle, and plinthite along profiles P1 and P2 (Figure 2) were defined to assess possible spatial variations (horizontal or vertical) regarding Fe accumulation and plinthite hardening (Martins et al., 2018a; Santos et al., 2022) in relation to the other redoximorphic features within each profile. In the upper plinthic horizons and in the main plinthic horizon, samples of soil matrix, mottle, and plinthite were collected in two positions: upper right position (Pst1 and Pst3) and lower left position (Pst2 and Pst4); in the base plinthic horizons, these samples were collected only in position 5 (Pst5) (lower right position) of profiles P1 and P2. Each position (Pst) sampled was demarcated with the aid of a metallic sampler with dimensions of 0.12 × 0.15 × 0.15 m (width, height, and length), which resulted in samples with a volume of 0.0027 m^3 in each Pst. From then on, the soil matrix (Figure 3a), mottle (Figure 3b), and plinthite (Figure 3c) were separated.

Considering the classic criteria for separation (color and consistency) recommended by technical manuals (IBGE, 2015; Santos et al., 2015) for each profile, five sets of soil matrix (5 Pst) and three sets of mottles (3 Pst) were separated in P1, as well as two sets of mottles in P2 (2 Pst) and five sets of plinthite (5 Pst) per soil profile. For matrix and mottle, each Pst comprised a single sample; for plinthite, each Pst comprised ten samples. In each profile, five samples (sets) of matrix, three samples (sets) of mottles in P1, and two samples (sets) of mottles in P2 were obtained. As for plinthite, 50 plinthite samples (five sets) were obtained in each profile. In total, 115 samples were evaluated (13 sets in P1 and 12 sets in P2).

After performing all separations of interest of soil matrix and redoximorphic features, the samples of each group and position were ground in an agate mortar and used to perform chemical and mineralogical determinations in each soil profile.

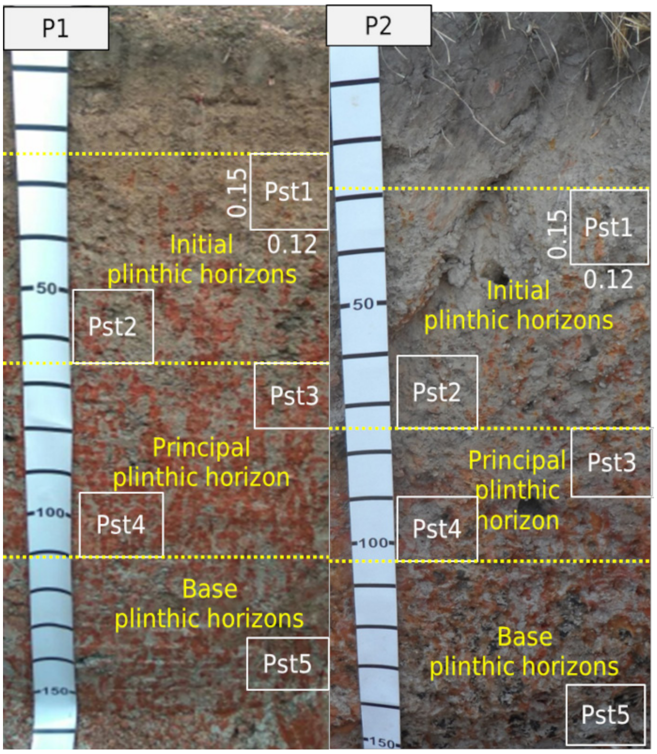

Figure 2. Scheme for collecting samples of redoxymorphic features in soil profiles P1 and P2. Pst: position.

X-ray fluorescence spectrometry analysis

To evaluate the total contents of the elements (all elements expressed in the form of oxides), X-ray fluorescence spectrometry (XRF) analyses were carried out on the samples crushed and ground in an agate mortar until they were in the form of powder (material that passed through a 0.053 mm mesh sieve). Two grams of each sample were used per position. Samples were placed in a standard sample holder with a bottom coated with 3.6 µm "mylar" polyester film, and then placed on a removable carousel with a capacity of 10 samples (Heberle, 2017). In this analysis, two readings were taken on each sample, considering the final average for each soil element. To evaluate the chemical elements contained in the soil matrix and in each feature, an overall average of all sampled positions was made.

Analysis by sulfuric acid attack

Plinthite samples were ground in an agate mortar and prepared for dissolution with sulfuric acid to identify and quantify the elements silicon (Si), aluminum (Al), iron (Fe), and titanium (Ti), either free or present in the structure of secondary minerals (Verdade, 1972). This procedure enabled the calculation of molecular relationships (Ki and Kr) to assess soil weathering stages. For this determination, samples were solubilized with 1:1 sulfuric acid (H_2SO_4), according to Teixeira et al. (2017).

Analysis from selective iron extractions

Plinthite samples were ground in an agate mortar and prepared for Fe extraction by sodium dithionite-citrate-bicarbonate (Fed) and ammonium acid oxalate (Feo). Analyses were carried out following the method of Teixeira et al. (2017). For data tabulation and graphing of different Fe extractions, means of the five positions for each redoximorphic feature were used.

Figure 3. Studied redoxymorphic features – (a): soil matrix; (b): mottle; (c): plinthite.

X-ray diffraction analysis

Clay fraction mineralogy in the matrix and in the different soil features in the positions (Pst 3 and Pst 4) was determined by X-ray diffraction (XRD) using a Shimadzu XRD 6000 diffractometer operated with Cu Kα radiation at 40 kV and 30 mA, as well as a graphite monochromator. Clay fraction was analyzed as unoriented and untreated powder samples at a speed of 1° min^{-1} 2θ and recorded in the range of 3 to 70° (2θ). In another treatment, clay samples were pretreated and deferrified using the DCB solution (Jackson, 1975). Saturation treatments were performed using potassium (K) and magnesium (Mg) in the form of oriented clay microaggregates (Jackson, 1975) at a rate of 0.7° min^{-1} 2θ and within a range of 3 to 35° 2θ. Samples saturated with K (KCl 1 mol L^{-1}) underwent successive heat treatments (25, 350, and 550 °C), and samples saturated with Mg ($MgCl_2$ 1 mol L^{-1}) were analyzed at room temperature, solvated with glycerol, and then analyzed at a speed of 0.7° min (2θ) within a range of 3 to 15° (2θ).

The criteria used to interpret the XRD and identify the minerals present in the clay fraction were based on interplanar spacing (d); on the behavior of the diffraction peak in relation to saturation and heat treatments, as presented in Brown and Brindley (1980), Jackson (1975) and Moore and Reynolds (1997); and on the behavior in treatments.

Statistics

Standard error of the mean was obtained by dividing the standard deviation of the sample by the square root of the number of observations of the soil matrix and each redoximorphic feature. Graphs, tables, their respective standard errors, and error bars with percentage (5 % significance) and trend lines were made using the Microsoft Excel 2010 program.

RESULTS

Chemical constitution and iron content in the soil matrix and the different redoximorphic features

Table 1 shows the total contents of chemical elements constituting the soil matrix and the redoximorphic features, expressed in the form of oxides and determined by X-ray fluorescence (XRF), with the average of the five positions sampled in each soil profile. Overall, the sum of Si (SiO_2), Al (Al_2O_3), and total Fe (Fe_2O_3) contents accounted for values above 96 % for the elements analyzed in the soil matrix and in all redoximorphic features in the two soil profiles, indicating the absolute predominance of these constituents. In particular, the amount of total Fe (Fe_2O_3) stands out, which is directly proportional to the development of more reddish colors and firmer consistency of the different features, being 4.71 and 3.69 % in the matrix; 8.76 and 7.94 % in the mottle; and 16.57 and 15.77 % in the plinthite of profiles P1 and P2, respectively. The element thus concentrates 3.51 and 4.27 times more in the plinthite in relation to the matrix, and 1.89 and 1.99 times more in the plinthite in relation to the mottle.

Table 1. Total chemical constitution of the soil matrix and redoximorphic features, determined by X-ray fluorescence (FRX)

Features[1]	SiO_2[2]	Al_2O_3	Fe_2O_3	TiO_2	MgO	K_2O	V_2O_5	ZrO_2	Others
	g kg^{-1}								
Profile 1 - *Plintossolo Argilúvico Distrófico típico* (Santos et al., 2018) / Plinthosol (IUSS Working Group WRB, 2022)									
Matrix	509.99±1.55	403.13±1.86	47.05±1.51	19.04±0.40	1.94±0.12	10.96±0.84	0.28±0.01	0.53±0.04	7.48±0.31
Mottle	488.36±4.84	384.15±2.23	87.57±6.38	16.94±0.47	2.10±0.09	12.33±0.71	0.40±0.03	0.44±0.05	7.71±0.22
Plinthite	459.92±14.75	342.26±10.25	165.65±9.58	14.11±0.25	2.08±0.17	11.00±0.71	0.42±0.03	0.45±0.05	9.31±0.65
Profile 2 - *Plintossolo Argilúvico Distrófico típico* (Santos et al., 2018) / Plinthosol (IUSS Working Group WRB, 2022)									
Matrix	599.00±6.13	326.18±3.59	36.89±4.97	17.20±0.38	2.41±0.14	10.05±0.34	0.21±0.01	0.67±0.02	7.40±0.16
Mottle	556.33±4.69	326.35±0.13	79.38±5.05	15.17±0.21	2.63±0.07	11.04±0.15	0.29±0.01	0.61±0.01	8.23±0.04
Plinthite	501.94±5.23	305.75±3.19	157.23±4.80	12.94±0.38	2.42±0.11	10.65±0.24	0.32±0.01	0.49±0.01	8.77±0.26

(1) Mean values of the five sampled positions for matrix and for each feature in the soil profiles. The numbers after the ± sign refer to the sample standard error for the matrix and for each element in each soil feature. (2) SiO_2: silicon dioxide; Al_2O_3: aluminum oxide; Fe_2O_3: iron oxide; TiO_2: titanium dioxide; MgO: magnesium oxide; K_2O: potassium oxide; V_2O_5: vanadium pentoxide; ZrO_2: zirconium dioxide.

Table 2 shows the average levels of chemical elements detected by sulfuric acid attack in the different features. Mean Fe values ranged from 141.67 and 112.45 g kg^{-1} in profiles P1 and P2, both for plinthite, a feature that also presented the lowest Ki value (1.25 in P1).

Mean iron contents determined by different methods in the redoximorphic features

Table 3 presents the results of the average Fe contents obtained by sulfuric acid attack (Fes), sodium dithionite-citrate-bicarbonate (Fed), and oxalate-ammonium acid (Feo) in the soil matrix and in the redoximorphic features. Overall, the data indicate the values of Fes, Fed, and Feo are higher in the plinthite feature, followed by the mottle, and finally the soil matrix, with higher values in profile P1 for all redoximorphic features under study. The Fed/Fes ratio was higher in P2, and Feo/Fed was equal between the two soil profiles.

Figure 4 shows the average Fe contents obtained by different methods in the soil matrix, mottle, and plinthite features. It is noteworthy the presence of higher values of iron in all its determination forms in the plinthite feature, followed by the mottle feature, and finally the soil matrix. As a rule, both profiles under study show a gradual variation of Fe contents in the different forms of determination, with Feo<Fed<Fes<Fet, which is logical considering the reach (at least theoretical) of each determination. Small exceptions occur between the values of Fes and Fet of the soil matrix of P2, which are practically equivalent, but higher in Fes.

Table 2. Characterization of the main chemical elements of the soil matrix and redoximorphic features as determined by sulfuric acid attack

Matrix and features[1]	SiO_2[2]	Al_2O_3	Fe_2O_3	TiO_2	Ki	Kr
	g kg^{-1}					
Profile 1 - *Plintossolo Argilúvico Distrófico típico* (Santos et al., 2018) / Plinthosol (IUSS Working Group WRB, 2022)						
Matrix	201.20±19.94	222.40±5.92	40.60±1.44	9.36±0.20	1.54	1.38
Mottle	251.00±28.88	228.00±10.26	63.00±4.00	9.27±0.03	1.87	1.59
Plinthite	209.67±13.01	214.56±4.97	141.67±7.90	7.84±0.19	1.73	1.25
Profile 2 - *Plintossolo Argilúvico Distrófico típico* (Santos et al., 2018) / Plinthosol (IUSS Working Group WRB, 2022)						
Matrix	164.60±6.51	191.40±23.87	38.20±3.72	7.36±0.19	1.46	1.30
Mottle	194.00±4.00	180.50±2.50	62.00±3.00	7.60±0.40	1.83	1.50
Plinthite	201.00±5.84	182.27±4.46	112.45±4.99	7.63±0.38	1.81	1.31

(1) Mean values of the five positions sampled for matrix and for each feature in the soil profiles. Ki=(SiO_2/Al_2O_3)x1.70 and Kr=(SiO_2/0.6)/(Al_2O_3/1.02)+(Fe_2O_3/1.60). The numbers after the ± sign refer to the sample standard error for each element in the matrix and in each soil feature. (2) SiO_2: silicon dioxide; Al_2O_3: aluminum oxide; Fe_2O_3: iron oxide; TiO_2: titanium dioxide.

Table 3. Average iron contents from the soil matrix and redoximorphic features, determined by sulfuric acid attack (Fes), sodium dithionite-citrate-bicarbonate (Fed), ammonium acid oxalate (Feo), and their ratios (Feo/Fed)

Matrix and features	Fes	Fed	Feo	Fed/Fes	Feo/Fed
	g kg^{-1}			-	-
Profile 1 - *Plintossolo Argilúvico Distrófico típico* (Santos et al., 2018) / Plinthosol (IUSS Working Group WRB, 2022)					
Matrix	40.60±1.44	9.44±1.31	0.30±0.04	0.23	0.03
Mottle	63.00±4.00	23.37±1.59	0.58±0.09	0.37	0.02
Plinthite	141.67±7.90	50.14±1.07	1.61±0.15	0.35	0.03
Profile 2 - *Plintossolo Argilúvico Distrófico típico* (Santos et al., 2018) / Plinthosol (IUSS Working Group WRB, 2022)					
Matrix	38.20±3.72	10.05±1.93	0.26±0.04	0.26	0.03
Mottle	62.00±3.00	24.00±2.00	0.44±0.01	0.39	0.02
Plinthite	112.45±4.99	47.21±1.32	1.56±0.14	0.42	0.03

Iron values refer to the averages of the five positions (Pst) sampled in the profiles P1 and P2 for the soil matrix and for each redoximorphic feature. Numbers after the ± sign refer to the sample standard error for each element in the matrix and in each soil feature.

Also noteworthy are the Feo values of the two profiles under study for the plinthite feature, which were equivalent to each other, with values considered very low in relation to the other Fe forms under study.

XRD identification of minerals present in the clay fraction of the redoximorphic features

Figure 5 shows the X-ray diffractograms of the deferrified, oriented, and treated clay samples, relative to the clay fraction of the soil matrix and the mottle and plinthite features. All samples under study presented the clay minerals vermiculite (V), mica (Mi), kaolinite (K), and gibbsite (Gb).

The XRD of soil matrix samples and redoximorphic features in powder form (unoriented and untreated) showed the predominance of the Fe hydroxide goethite (Gt) in both soil profiles (Figure 6). On the other hand, hematite (Hm) occurred to a lesser extent in the features.

Chemical elements extracted by sulfuric acid attack and Ki and Kr values in redoximorphic features

Figure 7 shows the contents of chemical elements and values of Ki and Kr indices obtained by sulfuric acid attack in the soil matrix and in each redoximorphic feature distributed by

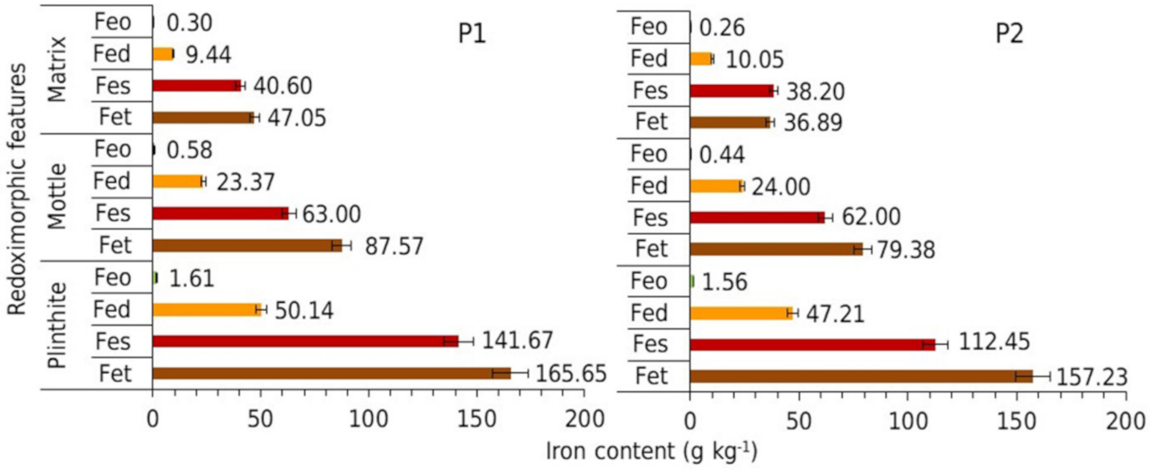

Figure 4. Mean values of the element iron extracted by different methods in the soil matrix and in the redoximorphic features of the studied profiles. Fet: X-ray fluorescence; Fes: sulfuric acid attack; Fed: dithionite-citrate-sodium bicarbonate; Feo: ammonium acid oxalate. Error bars refer to sample variability in percentage (5 % significance).

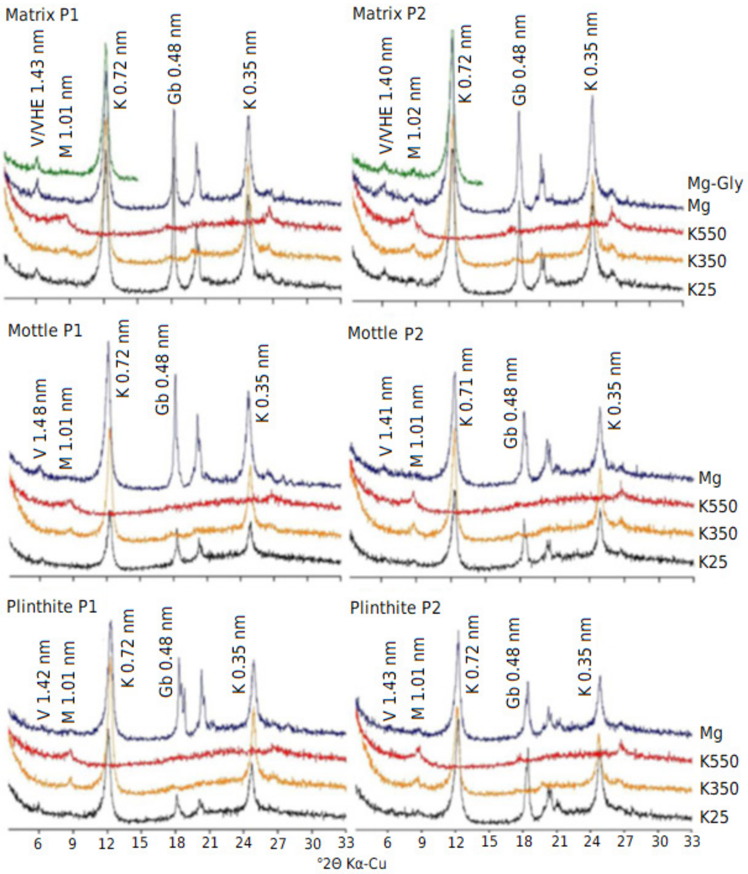

Figure 5. X-ray diffractograms of the deferrified, treated and oriented clay fraction of the soil matrix and of the redoximorphic features of the profiles. Samples were saturated with potassium (K) at room temperature 25 °C (K25), heated to 350 °C (K350) and 550 °C (K550) and saturated with magnesium (Mg) and magnesium+glycerol (Mg-Gly), V: vermiculite; Mi: mica; K: kaolinite; and Gb: gibbsite.

position (Pst) sampled from the P1 profile. Overall, the trend lines show that Si (SiO_2) and Al (Al_2O_3) levels increase from the initial position (Pst1) to the lower position (Pst5) in all features under study in profile P1. The same trend occurred for the values of Ki and Kr indices, indicating a higher degree of weathering in the upper positions for all features. As for the free Fe contents of this profile, the trend line does not show any regularity or similarity between the features or between the positions.

Results regarding the chemical elements determined by sulfuric acid attack and distributed by position (Pst) sampled from profile P2 (Figure 8) do not show either a defined logical trend for any of the elements nor weathering relationships for any of the redoximorphic features under study. The element Fe stands out, whose content increases in the soil matrix from Pst1 (28 g kg^{-1}) to Pst5 (49 g kg^{-1}) and decreases in the mottle from Pst4 (65 g kg^{-1}) to Pst5 (59 g kg^{-1}). In the plinthite, Fe content increases from Pst1 (111 g kg^{-1}) to Pst2 (126 g kg^{-1}), decreasing in Pst3 (118 g kg^{-1}), increasing again in Pst4 (125 g kg^{-1}), and decreasing again in Pst5 (114 g kg^{-1}), with values very close to those of Pst1.

Iron element in the soil matrix and plinthite features at different positions in the profiles

Figures 9 and 10 show Fed and Feo contents together with Fes contents and the Fed/Fes ratio in the different positions under study in each profile, within soil matrix features and in the plinthite. This analysis is important to evaluate the specific or isolated behavior of the high and low crystallinity (Fed) forms of iron that constitute the form that can be produced and concentrated in the soil as a direct consequence of the redox process.

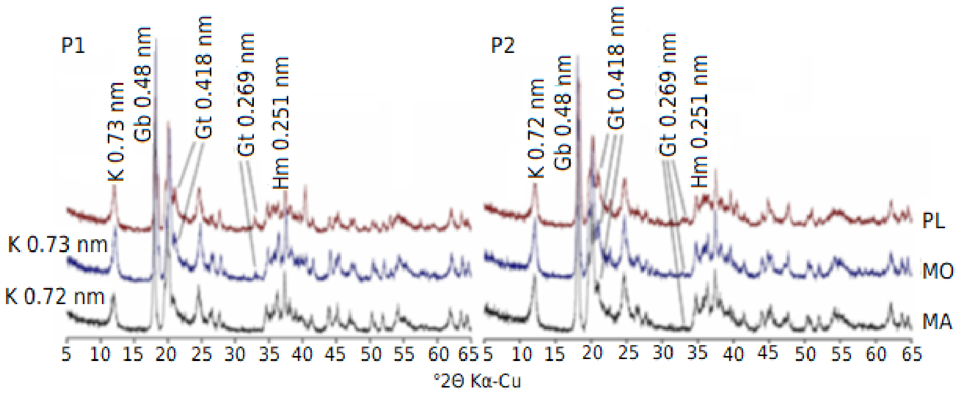

Figure 6. X-ray diffractograms of samples fragmented by the Instron device, crushed and ground until they are in powder form (powder), unoriented and untreated of the clay fraction of the soil matrix and of the redoximorphic features of the two profiles (P1 and P2). K: kaolinite; Gb: gibbsite; Gt: goethite, Hm: hematite. MA: soil matrix; MO: mottle; PL: plinthite.

Overall, there is no defined pattern of regular distribution in the forms of Fe in the plinthic horizons. Figure 9 indicates for the soil matrix and plinthite a trend of reduction in Fes contents from the initial plinthic horizons to the main plinthic horizon, with subsequent increase in these contents towards the base plinthic horizons, the same trend observed for Feo. In the opposite direction, Fed levels decrease from Pst1 to Pst5. The Fed/Fes ratio between the two features shows different patterns.

For the soil matrix in figure 10, Fes, Fed, Feo, and Fed/Fes values tend to increase from the initial plinthic horizons to the base plinthic horizons. In the case of plinthite, Fed and Fed/Fes values were practically constant, while Fes and Fed contents showed irregular distribution between the plinthic horizons analyzed in profile P2.

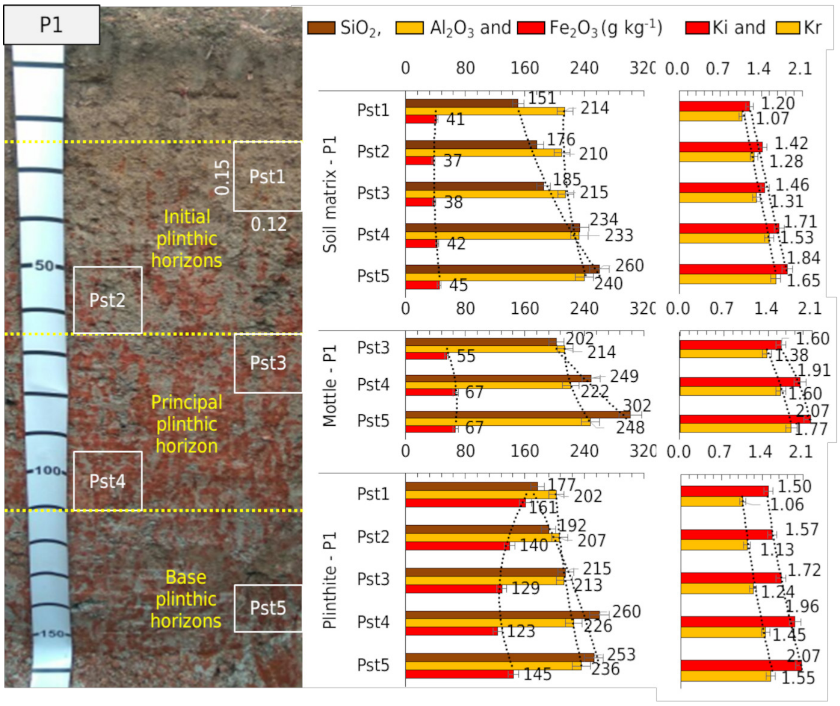

Figure 7. Contents of oxides of silicon (SiO_2), aluminum (Al_2O_3), iron (Fe_2O_3 or Fes) and Ki and Kr indices obtained in different positions (Pst) of the soil matrix and the redoximorphic features of the P1 profile (elements obtained by sulfuric acid attack). Error bars refer to sample variability in percentage (5 % significance).

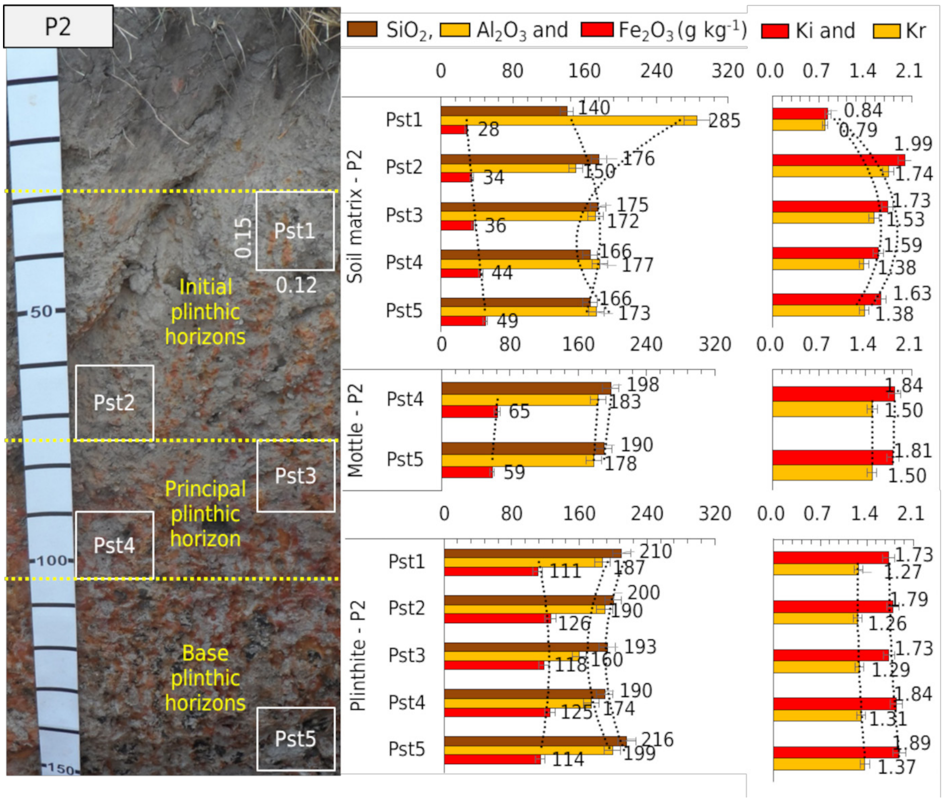

Figure 8. Contents of oxides of silicon (SiO_2), aluminum (Al_2O_3), iron (Fe_2O_3 or Fes) and Ki and Kr indices obtained in different positions (Pst) of the soil matrix and the redoximorphic features of the P2 profile. Error bars refer to sample variability in percentage (5 % significance).

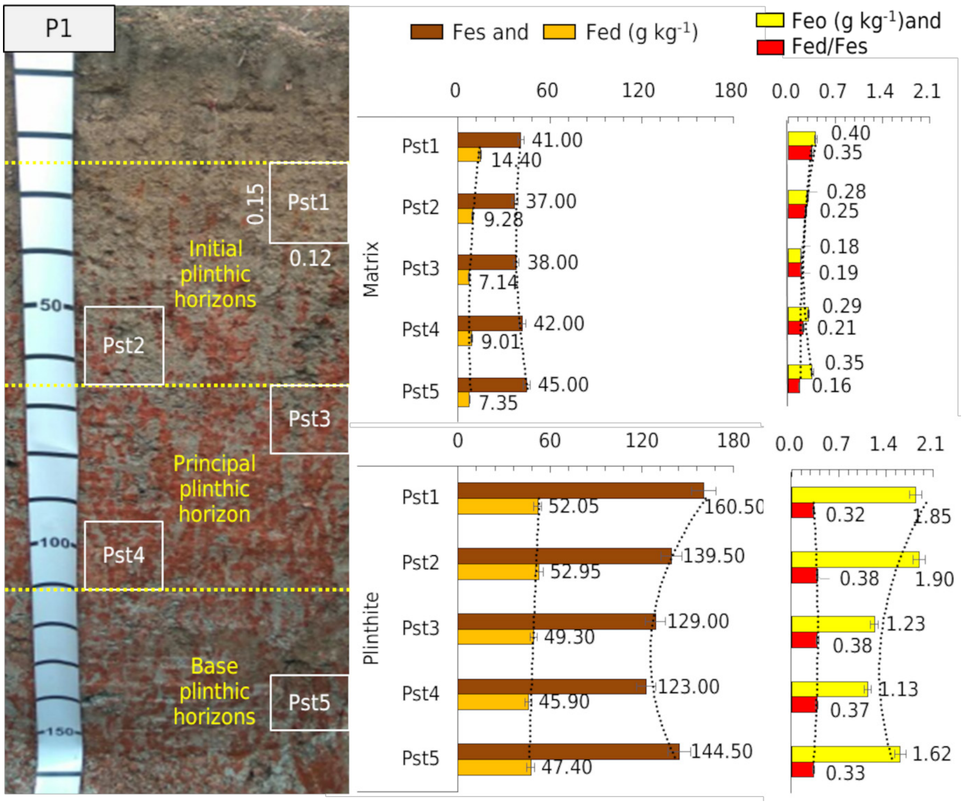

Figure 9. Iron contents obtained by sulfuric acid attack (Fes), sodium citrate-bicarbonate dithionite (Fed), ammonium acid oxalate (Feo) and Fed/Fes ratio obtained in different positions (Pst) of the soil matrix and the plinthite feature of the profile P1. Error bars refer to sample variability in percentage (5 % significance).

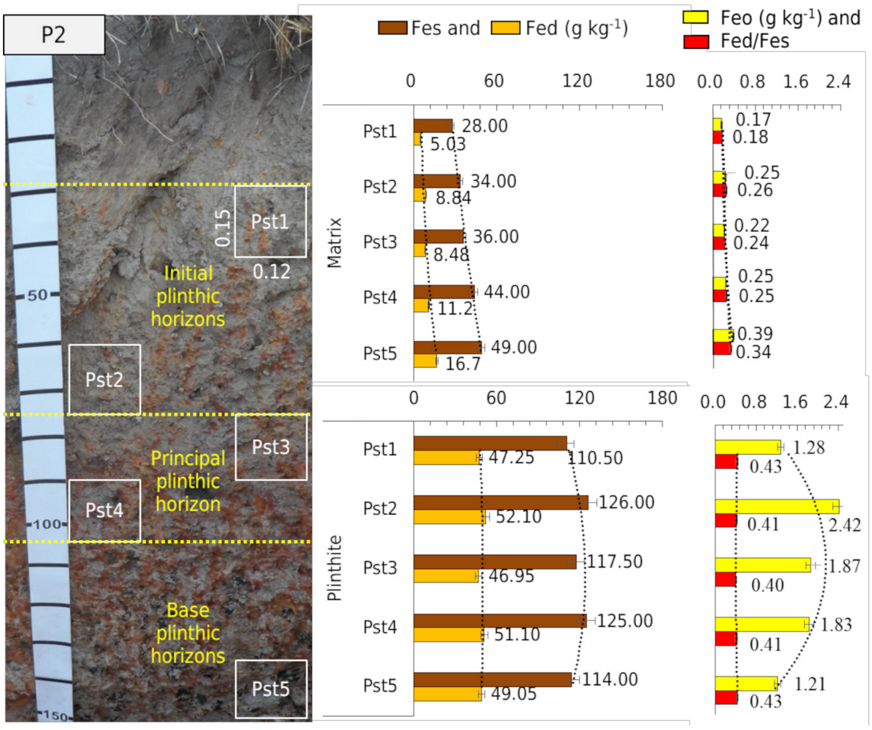

Figure 10. Iron contents obtained by sulfuric acid attack (Fes), sodium citrate-bicarbonate dithionite (Fed), ammonium acid oxalate (Feo) and Fed/Fes ratio obtained in different positions (Pst) of the soil matrix and the plinthite feature of the profile P2. Error bars refer to sample variability in percentage (5 % significance).

DISCUSSION

Iron in the soil matrix and in the different redoximorphic features

Elements Si (SiO_2), Al (Al_2O_3), and Fe (Fe_2O_3) are the most abundant in the redoximorphic soil features (Tables 1 and 2), corroborating other studies (Chauvel et al., 1987; Bravard and Righi, 1990; Roquin et al., 1990; Dubroeucq and Volkoff, 1998; Coringa et al., 2012). The sum of SiO_2, Al_2O_3, and Fe_2O_3 in table 1 makes up over 96 %, and in table 2, over 98 % of the total, in line with the values found by Martins et al. (2018a).

The differences in the levels detected between the methods in the two tables are due to the scope of each one of them, determined by their extraction power of each element in the samples. In other words, table 1 shows the values determined by XRF that encompass the elements present both in all mineral forms that make up the sample (primary and secondary minerals) and in the free form. In turn, table 2 shows the values of each element determined by sulfuric acid attack, either in the free form or present in the secondary minerals that constitute the clay fraction, and possibly in a small part of the silt fraction. The values of table 2 are always lower than those of table 1. The highest values of Si in table 1 in relation to those in table 2 refer to the amount of Si present in the form of quartz that constitutes the sand fraction, and in inherited micas and vermiculite, computed only by XRF.

Silicon (Si) values being higher in the matrix features (509.99 in P1 and 599.00 g kg^{-1} in P2), intermediate in the mottles (488.36 in P1 and 556.33 g kg^{-1} in P2), and lower in the plinthite (459.92 in P1 and 501.94 g kg^{-1} in P2) of both profiles (Table 1) is mainly due to the higher amount of Fe present in the plinthite (165.65 in P1 and 157.72 g kg^{-1} in P2) and mottle fractions (87.56 in P1 and 79.38 g kg^{-1} in P2), resulting from accumulation through the redox process. These results are relevant, as the specialized literature (Daniels et al., 1978; Díaz-Ortega et al., 2011; Soil Survey Staff, 2014; Santos et al., 2018) suggests that the plinthite feature is a material formed by Fe accumulation from a redox process, probably migrated from the matrix feature.

As for the total Al contents (XRF) presented in table 1, similar to Si, they are also higher in the matrix and mottle features than in the plinthite feature. This is partly because Al is an element of very low mobility (solubility) in weathering processes (Mason, 1971; Birkeland, 1974; Oliveira, 1998). Therefore, Al relatively increases in these features due to ions removal with greater solubility, especially Si (Mello and Perez, 2009; Buol et al., 2011). In line with it, Ki ratio values are much lower in the matrix feature (Table 2).

Regarding Fe content in the features, both tables 1 and 2 show higher contents in plinthite, followed by mottle and soil matrix. This pattern is in line with the literature, considering plinthite is the result of Fe concentration by the redox process, and mottles would be an intermediate phase of this process (Schwertmann and Kämpf, 1983; Eswaran et al., 1990; Payton et al., 1992; Lin et al., 2007; Tanner and Khalifa, 2010; Vepraskas, 2015). The other identified elements presented low values, totaling less than 5 % in all features and in the soil matrix. This seems quite natural considering that, in addition to already occurring normally in low concentrations in rocks and soils, many of these elements are very soluble and are removed from the system very quickly.

It should also be noted that the Fe values presented in tables 1 and 2 correspond to the average values of the contents occurring in all the positions (Pst1 to Pst5) of each profile and represent the general trend of each of them among the various features. In this context, the mottle feature is an intermediate feature between the matrix and the plinthite feature.

Iron forms in the soil matrix and in the mottle and plinthite features

Iron is the main agent of the redox process, forming plinthites by accumulation after being segregated and transported in redox processes (Daniels et al., 1978; Gong, 1999; Moreira and Oliveira, 2008) (Table 3; Figure 4). As we could observe in both soil profiles and for all determination methods used, Fe contents are always higher in the plinthite feature, followed by those in the mottle feature, and finally those in the soil matrix. According to the literature, this initially suggests that, in the case of a soil undergoing redox processes, the plinthite feature is formed by the accumulation of Fe from the mottle features and soil matrix (Duarte et al., 2000; Anjos et al., 2007; Tanner and Khalifa, 2010; IUSS Working Group WRB, 2022). From the values in figure 4 and considering the scope of each type of determination, it appears that the difference between Fet and Fes values refers to the Fe contained in primary minerals within each of the fractions. In the plinthite feature, these minerals have about 14.48 % of iron in P1 and 28.48 % of iron *[(1-(Fes/Fet))×100]* in P2.

According to IBGE (2015), the Fe contents determined by DCB (Fed) refer to the amount of Fe present in forms of high and low crystallinity (oxides and hydroxides). This value refers to the amount of Fe present in the features that could form in the soil as a result of a common redox process to promote the formation of plinthites or mottles (Singh and Gilkes, 1992; Díaz-Ortega et al., 2011). Moreover, the values determined by sulfuric acid attack (Fes) refer to the Fe present in all mineral components of the fine fractions of the soil (clay and silt), including secondary and oxide silicates (pedogenic Fe). Thus, the difference between the two values reveals the amount of Fe present only in secondary silicate minerals (Fe determined by sulfuric acid attack minus Fe extracted by DCB).

In this sense, it appears that of the 141.67 g kg^{-1} of Fe (Fes) present in the plinthite feature of P1, 91.53 g kg^{-1} {corresponding to 64.60 % *[(Fes-Fed)/Fes]×100}* occur in the structure of secondary silicate minerals, and only 35.40 % *[(1-(Fed/Fes))×100]* occur in the oxidic form, which is the part eventually accumulated by the redox process (Table 3 and Figure 4). In the case of P2, of the 112.45 g kg^{-1} of Fe (Fes) present in the plinthite feature, 65.24 g kg^{-1} (corresponding to 58.02 %) occur in the structure of secondary silicate minerals, and only 41.98 % is in the oxidic form. Thus, only 35.40 % of the Fe present in P1 plinthites and 41.98 % of the Fe present in P2 plinthites are in the form of high or low crystallinity oxides, which may or may not have been formed as a result of the redox processes occurring in the soils. According to Jamagne (1978), Soil Survey Staff (2014) and IUSS Working Group WRB (2022), redox processes are among the most common pedological processes.

Iron (Fe) stands out among the most active elements in this process (Trolard et al., 1993; Fiedler and Sommer, 2004). Once in the soil solution, under temporary hydromorphic conditions, Fe can be moved and reach a level or zone where it will be oxidized (Laveuf et al., 2012). Furthermore, it can be immobilized in the form of ferruginous concretions (van Breemen, 1988; Allen and Hajek, 1989; McKenzie, 1989). However, it must also be considered the raw material of the soils of the Araguaia river plain is formed by clay-sandy sediments of an alluvial-colluvial nature, belonging to the Phanerozoic Cenozoic Quaternary Pleistocene Gelasian, of the Cenozoic Cover, Bananal unit (RadamBrasil, 1981). With great probability, this material could have previously contained the element Fe in these oxidic forms (Fed and Feo). This evidences the possibility that a good part of the Fe detected is totally or partially inherited from the source material.

Therefore, most of the Fe in all redoximorphic features is included in the structure of primary minerals and some derivatives thereof. In P1, this amount is 79.94 % in the matrix, 73.31 % in the mottle, and 69.73 % in the plinthite *[(1-(Fed/Fet))×100]* (Tables 1 and 3). Similarly, in P2, the amount is 72.76 % in the matrix, 69.77 % in the mottle, and 70.07 % in the plinthite. Hence, there is a practically uniform distribution in the percentages of iron in the different points under study. This demonstrates the dynamics of this element in the matrix-mottle-plinthite direction does not provide accumulation in any of these points.

Identification of minerals present in the different features

Considering the source material of these soils, mica-bearing sediments of a colluvial-alluvial nature from the alteration of adjacent rocks, the micaceous minerals identified in their most complete form appear to be inherited from the source material. Moreover, their derivatives (vermiculite and mica-illite) may have been either locally formed or transported, in part or in whole. “True” micas are primary minerals and although they occur in soils, they are formed through a rock formation process (Resende et al., 2005), or more specifically in the magma crystallization process. In turn, the 2:1 phyllosilicates identified by XRD (Figure 5) in the clay fraction are formed by an alteration in the structure of true micas. This often occurs with the loss of some elements, mainly interlayer potassium with or without the introduction of aluminum polymers in the layers (VHEs). Another possibility is phyllosilicate neoformation from Si-rich solutions. In turn, all other identified mineral constituents, including oxidic ones (Figures 5 and 6), may at least in part have also been transported, as the sediments deposited for the formation of the source material of these profiles probably had varying degrees of weathering.

As it is currently a dissolution environment, determined by the region’s water regime, it is to be expected that micaceous minerals occur simultaneously in different stages of weathering, with coexisting species identified as true micas and some of its derivatives (illite, vermiculite, and VHEs). Figure 5 shows in some features, such as the soil matrix, which has higher concentration of clay minerals due to higher weathering, vermiculite (V) and VHE forms may coexist, given the pattern peaks in the range 1.40 to 1.43 in K treatments. Moura (2015) carried out a study near P2, identifying primary micas in the silt fraction, and illite and VHEs in the clay fraction.

Some authors have also detected minerals of the mica group and its derivatives in Plinthosols in Maranhão State (Anjos et al., 1995, 2007), in the sedimentary basin of the Solimões (Lima et al., 2006), in ferricretes in western Egypt (Tanner and Khalifa, 2010), and on lateritic material in northern Taiwan (Wada, 2004; Lin et al., 2005).

Iron element in the plinthite feature in different positions of the soil profiles

According to figures 7 and 8, there is no regular or logical distribution in the amounts of Fe, either in the determination of Fes (silicate form + oxidic form) or only in the crystalline or noncrystalline oxidic form (Fed) (Figures 9 and 10), that may show a tendency for Fe accumulation or translocation from redox reactionsin the soil profiles. These results differ from those found by Anjos et al. (1995) when evaluating soil samples in all plinthic horizons; by Coelho and Vidal-Torrado (2003) when evaluating samples from the plinthic and petroplinthic horizons; and by Anjos et al. (2007) when analyzing samples collected from each horizon, in which the authors detected an increase in Fed in depth.

Interpretation of figures 7 and 8 with respect to the variation of Fe, Si, and Al contents determined by sulfuric acid attack, present in the fine fraction of the soils (clay and part of the silt) of each feature, evidences that Fe contents in both profiles have a regular pattern in the soil matrix, increasing from the Pst2 position of P1 and the Pst1 (top) position of P2 to the base position Pst5.

This fact may indicate a loss of Fe from the top position, with consequent accumulation in the most basal part of the plinthic zone within the soil matrix due to redox processes. Several authors corroborate this affirmation (Daniels et al., 1978; Soil Survey Staff, 2014; Santos et al., 2018). Notwithstanding, it can also indicate migration of Fe-bearing silicate clay by eluviation and illuviation, or it can indicate that Fe-containing minerals are simply being destroyed, with this element leaving the upper part of this zone.

Mottle and plinthite features of both profiles do not show similar pattern, and there is no uninterrupted sequence in values, in any direction or orientation that can be considered regular or that can suggest any tendency of accumulation or concentration of Fe (Fes), for any of the reasons mentioned above.

Considering the other analyzed constituents, in P1 (Figure 7), Si contents mostly increase from the top to the bottom of the plinthic zone in all features and in the soil matrix. Meanwhile, Al contents also increase in the same direction, but in a much smaller proportion than Si. This fact results in Ki ratio values also increasing in the same direction from the top to the bottom of the plinthic zone, showing all features and the soil matrix are more weathered on the surface. This indicates a strong weathering front, from top to bottom, promoting the loss of Si and Fe, among other constituent elements.

This fact does not rule out a possible and small localized accumulation of oxidic Fe by the redox process, but it practically rules out the possibility of a significant migration of some type of Fe-bearing silicate clay (eluviation/illuviation). Granulometric analyses of these soil profiles presented in the studies by Martins et al. (2018a,b) reveal there is no significant addition of clay within this section, considered a “plinthic zone” or zone of plinthite occurrence of these profiles, which reinforces the impossibility of eluviation/illuviation.

In turn, in P2 (Figure 8), although Fe contents are also higher at the base of the matrix feature, the behavior of Si and Al in the clay fraction do not show or suggest a single weathering front in the profile with defined direction or orientation as in profile P1, nor do they suggest an eluviation/illuviation process. Rather, they suggest a nondirectional degradation process that happens simultaneously with a localized accumulation of Fe in the oxidic form.

Considering exclusively the data from the sulfuric acid attack, one can verify both profiles undergo a general destruction process of silicate minerals, mainly with the release of Fe and Si being more accentuated in the matrix feature, intermediate in the mottle, and lower in the plinthite, considering Fe contents still present therein. Based only on the values present in the matrix feature, weathering appears to be more intense in its upper portion. It is also worth noting that the mottle feature, considered intermediate in this process, occurs only in the lower parts of the “plinthic zone”. This indicates the possibility it has already been totally destroyed in the upper portion and has become part of the matrix feature.

Figures 9 and 10 show a considerable variability or irregularity in the arrangement of Fed values in the different positions under study, both within the soil matrix and in the plinthite feature. That is, there is no regular distribution or arrangement that shows or suggests any tendency of direction, position, segregation, or exclusive accumulation of this form of Fe, resulting from a redox process. On the other hand, the figures show a very close association of Fed values with the values detected by sulfuric acid attack (Fes). In samples with a higher concentration of Fed, there is also a higher concentration of Fes, which makes it possible to associate the higher levels of oxides (Fed) with the greater presence of Fe-bearing clay minerals in the fine fraction of each feature. At higher concentrations, these samples also provide higher levels of Fed when destroyed in relation to the probable localized accumulations of oxides by the redox process.

Mean values of the Fed/Fes ratio in plinthite of 0.35 in P1 and 0.42 in P2 (Table 3) suggest a reserve of iron in other groups of minerals, which can be released from the crystalline structure through weathering (Cornell and Schwertmann, 2006; Anjos et al., 2007). These values show only a part of the Fe considered pedogenic (Fes) is in the form of oxides (35 and 42 %, respectively), while most of it occurs in the crystalline structure of secondary minerals (vermiculite, illite, and VHEs). Therefore, if a part of this amount of iron (Fed) stems from accumulation through redox, it is supposed to happen in a very disorganized way and very small amounts, without a main tendency towards any direction or orientation.

Mechanisms of formation of redoximorphic features

Thus, the results already discussed in the topic Iron in the soil matrix and in the different redoximorphic characteristics, showing that Fe levels detected in all studied forms were highest in the plinthite feature, intermediate in the mottled feature and lowest in the soil matrix (Figure 4), corroborate with the theory that plinthites are Fe-rich materials in relation to the matrix and mottle (Daniels et al., 1978; Tanner and Khalifa, 2010; Díaz-Ortega et al., 2011; Soil Survey Staff, 2014; Santos et al., 2018).

Analysis of possible accumulations of oxidic Fe due to redox processes, which either create the forms with the highest Fe contents (mottles and plinthite) or partially contribute to their formation, shows no evidence of significant points or trends of Fe accumulation in this form. On the other hand, a clear process of destruction of plinthite features took place, with these features losing Fe and other elements, subsequently transforming into mottle and matrix features.

By exclusively observing the Fe content pattern in the soil matrix and in the different features and positions (Table 3; Figures 7, 8, 9 and 10), it appears that the matrix is the most weathered and the greatest contributor to the supply of elements for the formation of secondary minerals, mainly Fe. Furthermore, the higher contents of this element in the base positions of this feature indicate destruction occurs first in its upper portion and then increases in depth. Mottles presence only in the lower positions under study reinforces this theory. In turn, the contents in the different positions of the plinthite feature do not show a tendency towards the direction or orientation of this destruction. Thus, in the case of this feature destruction, other factors, such as the presence of different channels or microchannels (roots, organisms, pedogenic causes), which determine preferential paths for water movement, would certainly determine the different patterns of degradation fronts amid the mass of the initial feature as a whole (Figure 11). Martins et al. (2018a,b) observed considerable variations in the physical pattern of plinthite features in soils of the same plain of this study. These variations reflected differences in its constitution, which the authors attributed to the different degrees of maturity of these features.

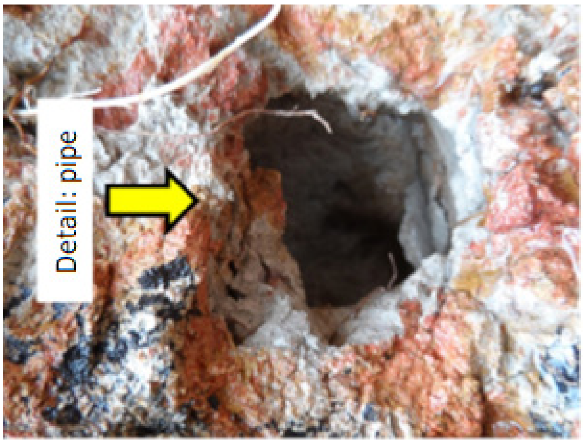

Figure 11. Detail of “pipe” water flow tubes present in the plinthic horizons of profiles P1 and P2.

When evaluating the forms in which Fe occurs in the soil matrix and in the mottle and plinthite features, based on the chemical data in tables 1 and 3 and the XRD results in figure 5, most of the Fe present in the plinthite feature {69.73 % in P1 and 70.07 % in P2, [*(1-(Fed/Fet))*×*100)*] (Tables 1 and 3)} is in the form of primary and secondary silicate minerals, *i.e.*, mica and derivatives, which are not formed during pedogenesis. Therefore, in these soils this feature presents Fe mostly in nonoxidic forms. In other words, these soils are not formed exclusively as a consequence of pedogenesis, corroborating the literature (Eze et al., 2014; Soil Survey Staff, 2014; Santos et al., 2018).

Finally, the very uniform and very low Feo/Fed ratio in all features (Table 3) and the low Feo contents in all positions within the profiles and in all profiles (Figures 9 and 10) lead us to consider that eventual transformations, whether from the formation of new minerals by redox or from decomposition of remaining minerals, are taking place at a very regular pace in terms of intensity and speed, given that the amount of crystalline Fe remains very high in relation to the amount of amorphous Fe in all situations. When studying soils with plinthite in Maranhão State, Brazil, Anjos et al. (1995) observed a Feo/Fed ratio around 0.03 in the plinthite feature, indicating the predominance of highly crystalline forms.

The absence of patterns of Fe contents (Fes, Fed, and Feo) verified in the plinthites in all positions of the profiles (Figures 9 and 10) and even within the same position, as well as the great variability of characteristics of this feature, such as degree of hardness - expressed by the applied compressive forces necessary for its breakage or rupture (Martins et al., 2018a) - are more easily understood by considering a generalized destruction of these features than probable localized accumulations of oxidic Fe.

For all these reasons it is reasonable to understand the formation of these redoximorphic features in these soils as a result of a great process of destruction of the original material deposited in these plains (colluvium-alluvial sediments). Plinthite features would thus be remnants of this material under constant weathering, releasing Fe, Si, and other mobile elements that are removed from the system through drainage.

CONCLUSIONS

Iron contents in all determined forms were always higher in the plinthite feature, intermediate in the mottle feature, and lower in the soil matrix feature. Most of the iron identified is not found in the structure of secondary minerals or as free iron, but is more likely in the structure of primary minerals such as micas and direct derivatives, detected by XRD.

Soil matrix feature sometimes has no traces of primary minerals (except quartz) and sometimes has very low amounts of this material, demonstrating that it is the most weathered feature of all features under study. Mottle and plinthite features under study are not the product of the classic segregation, mobilization, and iron accumulation due to redox processes.

Weathering process of the source material, which occurred gradually in an aqueous environment, contributed to the release of the iron used to form the iron oxides, with only part of the iron present in solution (35.40 % in P1 and 41.98 % in P2) being in the form of goethite and hematite. The observed characteristics result from these processes, which include iron and more mobile elements such as bases and silicon. These elements leave the system through drainage water, which a small part may eventually recombine to form new less complex minerals such as kaolinite and oxides.

DATA AVAILABILITY

All data was generated or analyzed in this study.

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