

Influence of parent material on mineralogy and iron forms in semiarid soils

Influência do material de origem na mineralogia e nas formas de ferro de solos semiáridos

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ABSTRACT - Soil mineralogy is a major determinant of soil physical, chemical, and biological properties. In semiarid environments, pronounced mineralogical heterogeneity requires specific management practices. This study characterized the mineralogy of the clay fraction of soils from rural communities in Mossoró, Rio Grande do Norte, Brazil, and evaluated the influence of parent material on mineralogical composition and pedogenetic development. Eight soil profiles were selected from 15 previously described profiles, and mineralogical analyses were performed on their diagnostic horizons. Iron forms were quantified by sulfuric acid digestion to determine iron associated with secondary minerals (Fes), dithionite-citrate-bicarbonate extraction to quantify free crystalline iron (Fed), and acid ammonium oxalate extraction to estimate low-crystallinity iron (Feo). The qualitative mineralogy of the clay fraction was determined by X-ray diffraction (XRD) using oriented slides subjected to the different chemical and thermal treatments. The soils were classified predominantly as mesoferric and hypoferric. XRD indicated the predominance of kaolinite, 2:1 phyllosilicates, probably illite and/or smectite, and iron oxides, with limited variation among parent materials. Under semiarid conditions, weathering and pedogenetic evolution, expressed by the mineral assemblage of the clay fraction and by iron forms, directly depended on parent material. These characteristics influence nutrient dynamics, natural soil fertility, and agricultural management in semiarid regions.

RESUMO - A mineralogia do solo é um dos principais determinantes das propriedades físicas, químicas e biológicas dos solos. Em ambientes semiáridos, a elevada heterogeneidade mineralógica exige práticas específicas de manejo. Este estudo caracterizou a mineralogia da fração argila de solos de comunidades rurais de Mossoró, Rio Grande do Norte, Brasil, e avaliou a influência do material de origem sobre a composição mineralógica e o desenvolvimento pedogenético. Oito perfis de solo foram selecionados a partir de 15 perfis previamente descritos, sendo realizadas análises mineralógicas nos horizontes diagnósticos. As formas de ferro foram quantificadas por digestão com ácido sulfúrico para determinação do ferro associado a minerais secundários (Fes), extração com ditionito-citrato-bicarbonato para quantificação do ferro livre cristalino (Fed) e extração com oxalato ácido de amônio para estimativa do ferro de baixa cristalinidade (Feo). A mineralogia qualitativa da fração argila foi determinada por difração de raios X (DRX) em lâminas orientadas submetidas a diferentes tratamentos químicos e térmicos. Os solos foram classificados predominantemente como mesoférricos e hipoférricos. Os difratogramas indicaram predominância de caulinita, filossilicatos 2:1, provavelmente illita e/ou esmectita, e óxidos de ferro, com variação limitada entre os materiais de origem. Os resultados demonstram que, em condições semiáridas, o intemperismo e a evolução pedogenética, expressos pela assembleia mineral da fração argila e pelas formas de ferro, são fortemente condicionados pelo material de origem. Essas características influenciam a dinâmica de nutrientes, a fertilidade natural dos solos e o manejo agrícola em regiões semiáridas.

Keywords: Mineralogical properties. Clay minerals. X-ray diffraction. Iron oxides.

Palavras-chave: Propriedades mineralógicas. Argilominerais. Difração de raios X. Óxidos de ferro.

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INTRODUCTION

The mineralogy of the clay fraction is one of the primary factors controlling the physical and chemical properties of soils and reflects the interaction among parent material, climate, and pedogenetic processes. Clay minerals are weathering products whose formation and transformation are directly associated with environmental conditions (ARAÚJO FILHO et al., 2017). In semiarid environments, such as the Northeast region of Brazil, pedogenesis is influenced by high temperatures and an irregular rainfall regime, generally resulting in limited leaching and the preservation of high-activity minerals with high base cation contents (OLIVEIRA et al., 2018).

In the Chapada do Apodi, data from the Exploratory-Reconnaissance Soil Survey of Rio Grande do Norte indicate the predominance of high-activity clay minerals, such as smectite and vermiculite, especially in less developed soils, such as Cambissolos (JACOMINE et al., 1971; ERNESTO SOBRINHO, 1979). However, more recent studies have documented the occurrence of low-activity minerals, such as kaolinite, in more developed soil classes, such as Argissolos and Latossolos (Brazilian Soil Classification System – SiBCS), suggesting greater

weathering intensity in specific environments and the influence of local factors, such as parent material and drainage conditions (FERREIRA et al., 2016; OLIVEIRA et al., 2018; LOPES et al., 2022).

Studies conducted in the Semi-arid region of Brazil show that the mineralogical composition of the clay fraction varies according to soil class and geological context. In the Chapada do Apodi, Latossolos and Cambissolos (SiBCS) contain mineral assemblages composed of hematite, goethite, kaolinite, and illite (LOPES et al., 2022). In other arid and semi-arid regions, such as central-western Morocco, complex assemblages involving palygorskite, vermiculite, and illite-smectite interstratified minerals have also been observed (OMDI; DAOUDI; FAGEL, 2018). Under semi-arid conditions, soil mineralogy is particularly complex because profiles often record the superposition of different pedogenetic environments, in which variations in the soil moisture regime and oxidation–reduction conditions influence both mineral stability and mineral transformation (OMDI; DAOUDI; FAGEL, 2018).

In addition to its pedogenetic significance, the mineralogy of the clay fraction is a determinant of soil functioning. Clay minerals directly influence attributes such as texture, structure, and aggregation (SHAHROKH; KHADEMI; ZERAATPISHEH, 2023), as well as fertility-related chemical properties, including cation exchange capacity, nutrient retention and availability, phosphorus adsorption, and pH buffering. These characteristics influence water retention, nutrient dynamics, and soil biological activity and are fundamental to fertility management and plant development (KOME et al., 2019). Therefore, understanding

the relationships between mineralogy and soil properties is essential for the sustainable use of soil resources, especially in semi-arid regions.

Despite advances in knowledge of semi-arid soil mineralogy, gaps remain in the integrated understanding of parent material, degree of weathering, and mineral assemblage at the local scale. The interactions among these factors in different geological contexts require investigation because the mineralogy of the clay fraction directly influences soil fertility and chemical behavior. In this context, this study evaluated the influence of parent material and degree of weathering on the mineralogical composition of the clay fraction and iron forms in representative soils of the Semi-arid region of Rio Grande do Norte to interpret the dominant pedogenetic processes and their implications for geochemical dynamics and potential agricultural use in these environments.

MATERIAL AND METHODS

Characterization of the study area

The study area encompassed 15 rural communities in Mossoró, Rio Grande do Norte, Brazil, where soil profiles were collected (Figure 1). The regional climate is classified as BSh, hot dry semi-arid (DUBREUIL et al., 2018), with mean annual rainfall between 580 and 770 mm (EMPARN data from 1992 to 2022) concentrated from February to May and predominant Hyperxerophilic Caatinga vegetation (ARAÚJO FILHO et al., 2017).

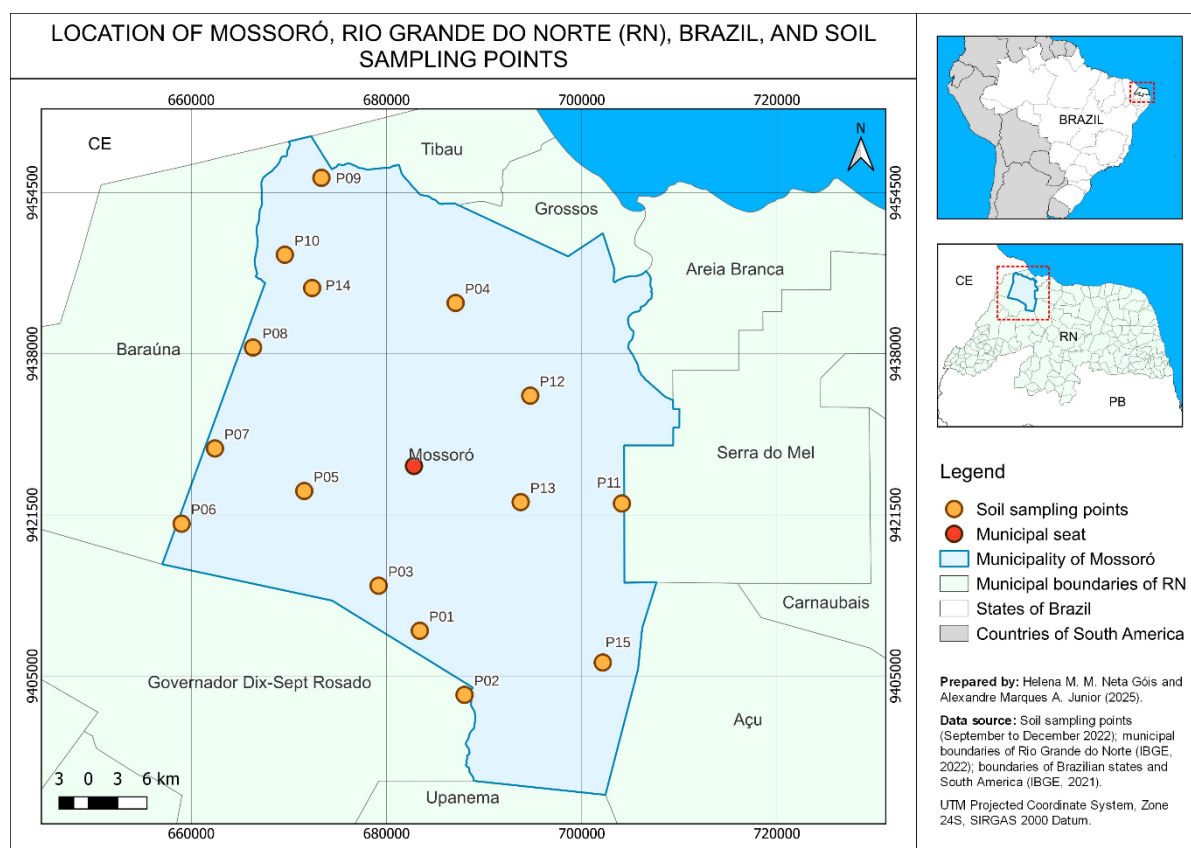


Figure 1. Location of the soil profiles evaluated in Mossoró, State of Rio Grande do Norte, Brazil.

The region has flat relief, with small areas of gently undulating terrain, and its hydrography includes two major rivers, the Apodi-Mossoró and Carmo rivers. The study area is in the Chapada do Apodi region and includes fluvial plains and terraces as geomorphological features. The area is dominated by carbonate rocks of the Jandaíra Formation,

sandstones and conglomerates of the Barreiras Group, sandy-clayey sediments and gravels corresponding to the Alluvial Deposits, and conglomeratic sandstones and sandstones corresponding to the Detrital-Lateritic Cover (DANTAS; MEDEIROS; CAVALCANTE, 2021) (Table 1).

Table 1. General geology of the soil profiles collected in Mossoró, State of Rio Grande do Norte, Brazil.

Group	Geomorphological domain	Geological units	Acronym	Collected profiles
Sedimentary formation	Chapada do Apodi	Jandaíra	K2adj	P1, P2, P5, P6, P7, P8, P14, and P15
		Barreiras	NQb	P4 and P11
		Detrital-Lateritic Cover	Q1dl	P9, P10, and P12
	Chapada do Apodi/ Fluvial plains and terraces	Alluvial Deposits	Q2a	P3 and P13

Description of the soil profiles and physical and chemical analyses

Fifteen soil profiles were opened in different rural communities in Mossoró, Rio Grande do Norte, Brazil, for the morphological, physical, and chemical descriptions. Soil samples from these profiles were collected, and morphological descriptions, including profile and environmental characteristics, followed the recommendations of the Manual of Soil Description and Collection in the Field (SANTOS et al., 2015). The profile characteristics considered were horizon sequence and depth, soil color determined with the Munsell® color chart, texture, structure, consistency, root presence, and transition between horizons. The environmental characteristics evaluated were rockiness, stoniness, relief, location, parent material, climate, vegetation cover, current land use, erosion, altitude, profile drainage, and other characteristics considered relevant.

Samples collected from each horizon were crumbled and passed through a sieve with a 2-mm mesh opening to obtain air-dried fine earth (TFSA) (TEIXEIRA et al., 2017) at the Soil, Water, and Plant Laboratory of the Federal Rural University of the Semi-Arid Region (LASAP-UFERSA). Physical and chemical analyses were performed in triplicate for each soil sample. Physical analyses included particle-size distribution, water-dispersible clay, bulk density, and particle density, according to the soil analysis manual organized by Teixeira et al. (2017).

Particle-size distribution was determined by the pipette method, using chemical and mechanical dispersion. In profiles with an effervescence reaction in the field, carbonates were completely removed using 10% hydrochloric acid (HCl) until effervescence ceased; subsequently, the samples were washed successively with water until neutral pH was reached, and particle-size analyses were then performed for these samples. Water-dispersible clay was determined using the same procedure, but without the chemical dispersant. Bulk density

was determined by the clod method or by the graduated-cylinder method, depending on soil texture, whereas particle density was determined using a volumetric flask (TEIXEIRA et al., 2017).

Chemical analyses were also performed according to Teixeira et al. (2017) and included pH in water and KCl (1:2.5), electrical conductivity (EC), and exchangeable cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). Na^+ and K^+ were extracted with Mehlich-1, and Ca^{2+} and Mg^{2+} were extracted with 1 mol L⁻¹ KCl; their concentrations were determined by flame photometry for sodium (Na^+) and potassium (K^+) and by atomic absorption spectrophotometry for calcium (Ca^{2+}) and magnesium (Mg^{2+}). Aluminum (Al^{3+}) was extracted with 1 mol L⁻¹ KCl (pH 7.0) and quantified by volumetric titration with 0.025 mol L⁻¹ NaOH. Available phosphorus (P) was extracted by the Mehlich-1 method and quantified by UV-Vis spectrophotometry. Potential acidity ($\text{H} + \text{Al}$) was extracted with 1 mol L⁻¹ calcium acetate (pH 7.0) and determined by volumetric titration with 0.025 mol L⁻¹ NaOH.

The calcium carbonate equivalent (CaCO_3) was determined by titrating the samples with standardized 0.5 mol L⁻¹ hydrochloric acid (HCl), followed by titration with standardized 0.025 mol L⁻¹ NaOH (TEIXEIRA et al., 2017). Total organic carbon was quantified by titrating the remaining 0.167 mol L⁻¹ potassium dichromate with 0.2 mol L⁻¹ ammonium ferrous sulfate. The variables used and the attributes determined for the profile horizons are shown in Table 2.

Based on the morphological observations and physical and chemical analyses, the 15 soil profiles were classified to the fourth categorical level according to the Brazilian Soil Classification System – SiBCS; (SANTOS et al., 2025) and the World Reference Base for Soil Resources (IUSS WORKING GROUP WRB, 2022) (Table 3). Soil descriptions and discussion in this article follow SiBCS terminology, with WRB equivalents provided in Table 3.

Table 2. Physical and chemical attributes of horizons in the soil profiles studied in Mossoró, State of Rio Grande do Norte, Brazil.

Horizon (depth, cm)	TC	pH in water	EC ds m ⁻¹	TOC g kg ⁻¹	P mg kg ⁻¹	Na ⁺ -----	Al ³⁺ cmolc kg ⁻¹ -----	H + Al	CEC
P1 – LUVISSOLO CRÔMICO Pálico arênico abrupto									
A1 (0–11)	Sand	6.57	0.05	13.25	3.46	0.17	0.00	1.00	11.48
Bt (104–126+)	Sandy clay	5.27	0.02	5.87	1.24	0.20	0.71	3.00	20.72
P4 – LUVISSOLO CRÔMICO Pálico arênico abrupto									
A1 (0–22)	Sand	4.98	0.05	2.69	2.05	0.17	0.42	0.40	4.71
Bt (108–171+)	Sandy loam	4.75	0.02	2.13	1.48	0.12	0.66	1.60	10.57
P7 – CAMBISSOLO HÁPLICO Ta Eutrófico argissólico									
A (0–16)	Sandy clay loam	6.27	0.03	7.99	1.60	0.11	0.00	1.30	16.06
Bi1 (63–125)	Sandy clay	5.33	0.03	3.80	1.19	0.11	0.33	1.70	12.99
P9 – LUVISSOLO CRÔMICO Pálico arênico abrupto									
Ap (0–20)	Sand	4.89	0.12	6.14	6.02	0.23	0.24	1.40	10.49
Bt (95–170+)	Sandy loam	4.31	0.18	1.88	1.44	0.32	0.19	0.80	6.16
P10 – LUVISSOLO CRÔMICO Pálico arênico abrupto									
A (0–15)	Sand	7.20	0.08	8.84	6.67	0.11	0.00	0.20	8.12
Bt2 (78–107+)	Sandy clay loam	6.59	0.02	4.41	1.55	0.11	0.00	0.60	11.01
P11 – ARGISSOLO VERMELHO–AMARELO Eutrófico abrupto									
A1 (0–15)	Loamy sand	4.63	0.03	8.74	2.52	0.11	0.38	1.60	4.84
Bt (68–177+)	Sandy clay	4.52	0.02	6.81	1.37	0.11	0.99	1.50	4.24
P12 – PLINTOSSOLO ARGILÚVICO Eutrófico arênico abrupto									
A (4–54)	Sand	5.88	0.01	4.83	2.38	0.11	0.38	0.40	5.37
Bt2 (113–148+)	Sandy clay loam	5.50	0.04	4.15	1.44	0.27	0.19	1.20	15.53
P13 – VERTISSOLO HÁPLICO Carbonático solódico									
Apk (0–16)	Silty clay loam	7.11	0.32	8.55	23.66	1.64	0.00	1.10	27.35
Ckn2 (34–102+)	Clay	7.60	2.09	6.32	68.27	10.14	0.00	0.90	26.34

TC = textural class; EC = electrical conductivity; TOC = total organic carbon; H + Al = potential acidity; CEC = cation exchange capacity at pH 7.0.

Table 3. Classification of the soils evaluated in Mossoró, State of Rio Grande do Norte, Brazil, according to the Brazilian Soil Classification System (SiBCS) and the World Reference Base for Soil Resources (WRB).

Profile	System	Soil classification (SiBCS / WRB)	SiBCS Acronym
Luvisolos / Luvisol			
P1	SiBCS	LUVISSOLO CRÔMICO Pálico arênico abruptico	TCp
	WRB	<i>Abrupt LUVISOL (arenic hypereutric)</i>	
P4	SiBCS	LUVISSOLO CRÔMICO Pálico arênico abruptico	
	WRB	<i>Abrupt LUVISOL (arenic hypereutric)</i>	
P9	SiBCS	LUVISSOLO CRÔMICO Pálico arênico abruptico	
	WRB	<i>Abruptic Chromic LUVISOL (arenic hypereutric ochric)</i>	
P10	SiBCS	LUVISSOLO CRÔMICO Pálico arênico abruptico	
	WRB	<i>Abruptic Chromic LUVISOL (arenic hypereutric ochric)</i>	
Cambissolos / Cambisol			
P5	SiBCS	CAMBISSOLO HÁPLICO Carbonático típico	CXk
	WRB	<i>Leptic Calcaric Eutric CAMBISOL (ochric)</i>	
P6	SiBCS	CAMBISSOLO HÁPLICO Ta Eutrófico lítico	CXve
	WRB	<i>Leptic Calcaric Eutric CAMBISOL (ochric)</i>	
P7	SiBCS	CAMBISSOLO HÁPLICO Ta Eutrófico argissólico	
	WRB	<i>Eutric CAMBISOL (ochric)</i>	
P14	SiBCS	CAMBISSOLO HÁPLICO Ta Eutrófico argissólico	CXk
	WRB	<i>Eutric CAMBISOL (ochric)</i>	
P15	SiBCS	CAMBISSOLO HÁPLICO Carbonático leptofragmentário	
	WRB	<i>Leptic Calcaric Eutric CAMBISOL (alcalic ochric)</i>	
Neossolos / Leptosol or Fluvisol			
P2	SiBCS	NEOSSOLO LITÓLICO Carbonático típico	RLk
	WRB	<i>Calcaric Eutric LEPTOSOL (ochric)</i>	
P3	SiBCS	NEOSSOLO FLÚVICO Ta Eutrófico gleissólico	RYve
	WRB	<i>Gleyic Eutric FLUVISOL (arenic ochric)</i>	
P8	SiBCS	NEOSSOLO LITÓLICO Eutrófico fragmentário	RLe
	WRB	<i>Eutric LEPTOSOL (ochric)</i>	
Argissolo / Lixisol			
P11	SiBCS	ARGISSOLO VERMELHO-AMARELO Eutrófico abruptico	PVAe
	WRB	<i>Abruptic LIXISOL (hypereutric ochric magnesian)</i>	
Plintossolo / Plinthosol			
P12	SiBCS	PLINTOSSOLO ARGILÚVICO Eutrófico arênico abruptico	FTe
	WRB	<i>Haplic PLINTHOSOL (eutric ochric magnesian)</i>	
Vertissolo / Vertisol			
P13	SiBCS	VERTISSOLO HÁPLICO Carbonático solódico	VXk
	WRB	<i>Protosodic Calcic VERTISOL (hypereutric ochric)</i>	

Iron oxide determination

Iron oxides were quantified in the clay fraction of the surface and diagnostic horizons of each soil class. Total iron was initially determined by sulfuric digestion according to Vettori (1969), which quantifies iron present in secondary minerals (Fes). Crystalline iron in iron oxides (Fed) was obtained after extraction with a dithionite–citrate–bicarbonate solution, according to Mehra and Jackson (1960). Low-crystallinity iron (Feo) was obtained using 0.2 mol L⁻¹ acid ammonium oxalate solution in the dark. The Feo/Fed and Fed/Fes ratios were calculated from the extracted Fe contents. After extraction, iron forms were quantified by atomic absorption spectrophotometry.

Mineralogical analyses of the soil profiles

Mineralogical characterization was performed on the clay fraction of the diagnostic horizons of eight of the 15 collected profiles. These profiles were selected based on the physical and chemical differences observed among profiles. In addition, profiles classified as Neossolos (SiBCS), which have weakly developed pedogenetic features, were used as an exclusion criterion. Chemical dispersion with 0.0025 mol L⁻¹ sodium hexametaphosphate and mechanical dispersion with a Wagner shaker for 16 h were used for clay separation. The clay fraction was separated by siphoning, and this procedure was repeated several times until the clay fraction was completely removed (TEIXEIRA et al., 2017). After drying, the clay samples were pulverized in an agate mortar and

sieved through a stainless-steel sieve (212 μm ; 65 mesh).

Subsequently, the clay samples were treated with sodium dithionite to remove iron oxides and subjected to saturation treatments with potassium (K^+) and magnesium (Mg^{2+}), followed by solvation with ethylene glycol. After the treatments, oriented slides were prepared with natural clay, K^+ -saturated clay heated to 550 $^{\circ}\text{C}$, and Mg^{2+} -saturated clay solvated with ethylene glycol, and the slides were analyzed at room temperature. All pretreatment, magnesium saturation, and potassium saturation procedures were performed according to the methods proposed in the Manual of Soil Analysis Methods (TEIXEIRA et al., 2017) to assist in the identification of different clay minerals.

Mineral phases were identified by X-ray diffraction (XRD), using a benchtop XRD instrument (Rigaku Miniflex II desktop X-ray diffractometer). The equipment was operated with a copper tube, 30 kV voltage, 15 mA current, and continuous scanning. The clay samples were oriented as smears by rubbing them with a glass slide on the analysis surface. Peaks were identified using Origin software, version 2021, and minerals were identified according to Chen (1977).

RESULTS AND DISCUSSION

Iron oxides in the profiles

Total iron contents (Fes) were higher than 80 g kg^{-1} Fe_2O_3 in most profiles and ranged from 82.25 to 162.48 g kg^{-1} , allowing their classification as mesoferric soils according to the criteria established by Santos et al. (2025) (Table 4). In contrast, profiles P1, P4, P7, P9, and P12 had values between 54.17 and 75.41 g kg^{-1} Fe_2O_3 and were classified as hypoferric (SANTOS et al., 2025). This variation reflects differences in parent material composition and in the intensity of active pedogenetic processes. Profiles P10 (Luvisolo; 152.51 g kg^{-1}), P6 (Cambissolo; 146.64 g kg^{-1}), P14 (Cambissolo; 162.48 g kg^{-1}), P2 (Neossolo; 162.25 g kg^{-1}), P8 (Neossolo; 143.91 g kg^{-1}), and P13 (Vertissolo; 153.32 g kg^{-1}) had the highest Fes contents in both surface and subsurface horizons (Table 4).

Higher Fes concentrations were observed in the surface horizons, possibly because of the relative concentration of iron resulting from the selective loss of bases and silica. In Cambissolos, however, the highest contents occurred in Bi subsurface horizons, indicating incipient mineral alteration and relative iron accumulation, which are characteristic of soils in early pedogenetic development. This pattern may be associated with high cation exchange capacity, indicating lower leaching intensity, greater cation retention, and preservation of parent material characteristics.

In profile P14, the high Fes contents, together with low dithionite-extracted iron (Fed) values, resulted in very low Fed/Fes ratios (Table 4), indicating the predominance of structural iron incorporated into slightly weathered primary or secondary minerals and a strong influence of parent material with a low degree of pedogenetic transformation. In the surface horizon, the Feo/Fed ratio greater than 1 indicates the predominance of low-crystallinity iron forms, possibly associated with organic matter or poorly crystallized oxides, such as ferrihydrite.

The highest free crystalline iron (Fed) contents were observed in profile P10, with 120.83 g kg^{-1} in the surface horizon and 119.03 g kg^{-1} in the subsurface horizon. High Fed values were also observed in profiles P5 (65.46 g kg^{-1}), P6 (64.94 g kg^{-1}), and P8 (65.98 g kg^{-1}) (Table 4). These results indicate a greater proportion of more crystalline pedogenic iron oxides, possibly associated with greater environmental stability and a longer duration of weathering processes.

Low-crystallinity iron (Feo) contents were relatively low and ranged from 0.09 to 6.53 g kg^{-1} (Table 4), indicating the predominance of more stable and crystalline iron forms in most profiles. This pattern is consistent with semiarid conditions, in which the lower intensity of hydration, dissolution, and precipitation processes limits the formation and preservation of poorly crystalline oxides.

The distribution of the different iron forms reflects the interaction between parent material and degree of weathering. Whereas total iron contents reflect lithological control, the proportion of crystalline to poorly crystalline forms indicates the intensity of pedogenetic processes and local environmental conditions.

More clayey soils developed from the Jandaíra Formation had higher Fes and Fed contents than the sandy soils of the Barreiras Group, indicating the combined control of parent material and texture on iron retention and concentration in the profile because finer fractions favor greater specific surface area and greater retention capacity for mineral constituents. Similar results were reported by Inda, Fink and Santos (2018) in a study of pedogenic iron oxides in soils derived from sedimentary rocks in the state of Acre, Brazil.

Although this is not a typical pattern of pedogenetic evolution, the high Fes and Fed values observed in Cambissolos, Neossolos, and Vertissolos can be explained by the presence of ferromanganese concretions, which are frequently found in these soils. In these features, iron is concentrated in more stable forms, increasing total contents and extractable fractions regardless of the degree of profile development. High Fed values were also reported by Lopes et al. (2022) in Cambissolos of sedimentary origin in the Chapada do Apodi, indicating the atypical nature of these findings. Similarly, significant Fes and Fed contents were identified by Rêgo (2022) in Cambissolos in a study of soil genesis in the Potiguar Basin and were attributed to the occurrence of ferromanganese concretions along the profiles.

In contrast, the lower iron contents observed in more developed soils, such as Argissolos, can be explained by the nature of the parent materials, particularly those of the Barreiras Group and Detrital-Lateritic Cover, which are composed predominantly of iron-poor sandstones. This interpretation was corroborated by Correa et al. (2008) and Rêgo et al. (2016), who reported low iron oxide contents in soils developed from these materials. This pattern is also related to the physical and chemical attributes of these soils, which are characterized by a sandier texture, lower cation exchange capacity, and lower base saturation values, favoring leaching and iron removal during pedogenetic evolution. This pattern was also observed in sandier Luvisols derived from these materials, which had low iron contents, reinforcing the influence of parent material on the dynamics of this element.

Table 4. Iron content extracted by sulfuric digestion and expressed as Fe_2O_3 (Fes), iron content extracted with sodium dithionite-citrate-bicarbonate solution (Fed), and iron content extracted with acid ammonium oxalate solution (Feo) in the diagnostic horizons of the soil profiles evaluated in Mossoró, State of Rio Grande do Norte, Brazil.

Profiles	Horizon (depth, cm)	Fes	Fed	Feo	Fed/Fes	Feo/Fed
		----- g kg ⁻¹ -----				
Luvissolos						
P1	A (0–11)	75.41	15.74	0.09	0.21	0.01
	Bt (104–126)	82.25	31.44	1.58	0.38	0.05
P4	A1 (0–22)	65.66	3.67	2.52	0.06	0.68
	Bt (108–171)	54.17	2.51	0.36	0.05	0.14
P9	Ap (0–20)	59.22	4.31	5.15	0.07	1.19
	Bt (95–170)	72.34	4.52	0.43	0.06	0.09
P10	A (0–15)	152.51	120.83	4.71	0.79	0.04
	Bt2 (78–107)	133.72	119.03	1.23	0.89	0.01
Cambissolos						
P5	Ak (0–6)	127.46	65.46	2.35	0.51	0.04
	Bi (6–22)	139.43	61.53	2.19	0.44	0.04
P6	Ak (0–5)	141.35	62.13	1.48	0.44	0.02
	Bi2 (19–35)	146.64	64.94	0.86	0.44	0.01
P7	A (0–16)	110.22	7.17	0.72	0.07	0.10
	Bi1 (63–125)	95.99	5.41	5.63	0.06	1.04
P14	A (0–12)	162.48	1.29	1.88	0.01	1.45
	Bi2 (83–120)	114.88	3.52	1.27	0.03	0.36
P15	A $\bar{k}$ (0–15)	131.42	4.62	2.98	0.04	0.65
	Bik (15–42)	126.19	5.48	1.84	0.04	0.34
Neossolos						
P2	A $\bar{k}$ (0–19)	137.48	55.99	2.74	0.41	0.05
	Crk (19–40)	162.25	5.78	2.70	0.04	0.47
P3	A1 (0–15)	139.96	5.74	3.82	0.04	0.67
	C5g (105–123)	116.59	5.22	5.89	0.04	1.13
P8	A (0–11)	143.91	6.92	2.36	0.05	0.34
	Cr (11–45)	140.98	65.98	5.05	0.47	0.08
Argissolo						
P11	A1 (0–15)	119.16	6.92	2.30	0.06	0.33
	Bt (68–177)	125.41	5.58	1.45	0.04	0.26
Plintossolo						
P12	A (4–54)	73.89	5.08	6.53	0.07	1.29
	Btf2 (113–148)	109.03	1.76	2.30	0.02	1.31
Vertissolo						
P13	Ap $\bar{k}$ (0–16)	153.32	1.84	3.95	0.01	2.15
	C $\bar{k}$ 1 (11–34)	144.74	1.20	3.52	0.01	2.94

Iron oxides are sensitive indicators of environmental conditions, especially temperature and moisture (BIGHAM; FITZPATRICK; SCHULZE, 2002). In semiarid environments, the combination of high temperatures and low precipitation directly influences iron oxide formation, transformation, and stability. Limited water availability reduces leaching and favors the relative accumulation of iron in the profile, whereas high temperatures promote the dehydration of poorly crystalline forms and favor the formation of more crystalline oxides, such as hematite, which is responsible for the reddish color of soils (CAI et al., 2021).

According to Melo et al. (2020), hematite formation is favored by high temperature, low water activity, pH close to neutrality, and low organic matter contents, whereas goethite tends to form in more humid environments, with higher organic carbon content and pH farther from neutrality. Therefore, the pedoclimatic conditions typical of the Semiarid region of Brazil contribute to the predominance of more crystalline iron oxides, reflecting both the formation environment and the degree of mineral stability.

The Fed/Fes ratio ranged from 0.01 to 0.89, whereas the Feo/Fed ratio ranged from 0.01 to 2.94 (Table 4). These indices provide important information on the distribution and degree of crystallinity of iron forms in the evaluated soils.

The highest Feo contents occurred in the surface horizons and were associated with higher organic matter contents in these horizons. The interaction between organic compounds and iron released during weathering reduces the crystallization of pedogenic iron oxides and favors the formation of poorly crystalline forms (ANJOS et al., 2007; OLIVEIRA et al., 2018). This pattern is corroborated by the higher Feo/Fed ratios observed at the surface, indicating the relative predominance of these forms.

According to Anjos et al. (2007), the Fed/Fes ratio can be interpreted as an index of the iron reserve still present in the structure of weatherable primary and secondary minerals, which can be transformed into oxides during weathering. Comparison of the values obtained in this study with those reported by Oliveira et al. (2024) indicates that, in most evaluated soils, a significant fraction of iron remains structurally incorporated, indicating intermediate stages of pedogenetic evolution.

The Feo/Fed ratio is widely used as a qualitative indicator of the degree of crystallinity of iron oxides and, indirectly, of the degree of weathering. Values lower than 0.05 indicate the predominance of more crystalline oxides, which are typical of more developed soils, whereas higher values reflect a greater proportion of poorly crystalline forms associated with environments with a lower degree of pedogenetic evolution (ANJOS et al., 2007; CAMÊLO et al., 2017). However, Anjos et al. (2007) emphasized that this ratio is strongly influenced by parent material and pedoclimatic conditions and should be interpreted together with the environmental and geological context of the soils.

Overall, the results indicate that the distribution and occurrence forms of iron in the studied soils result from the interaction among parent material, texture, climatic conditions, and degree of weathering, supporting the use of these attributes as fundamental indicators of soil genesis and functioning in semiarid environments.

Mineralogical composition of the profiles

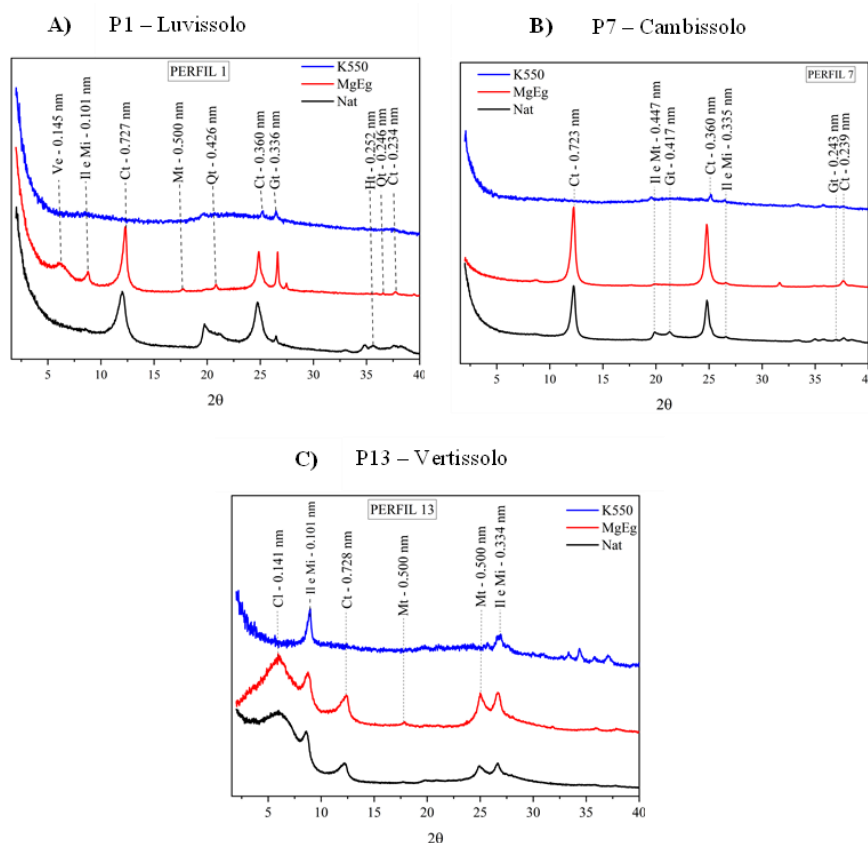
X-ray diffraction (XRD) analysis of the clay fraction indicated a complex mineral assemblage resulting from the interaction between parent material and pedogenetic processes. In profiles from the Jandaíra Formation (P1 and P7) and the Alluvial Deposits (P13), 2:1 clay minerals predominated, especially minerals of the smectite group, including montmorillonite, with additional occurrence of vermiculite, illite, and micas (Figures 2a, 2b, and 2c).

This pattern reflects parent material control because soils derived from limestone tend to contain abundant 2:1 clay minerals, particularly smectites (ARAÚJO FILHO et al., 2017). These minerals are typical of environments with high base saturation and low leaching intensity, which are conditions frequently associated with soils such as Vertissolos. Therefore, the identification of well-defined montmorillonite peaks in the evaluated Vertissolo profile corroborates the strong lithological influence and the geochemical conditions favorable to montmorillonite formation and/or preservation.

According to Kämpf and Curi (2003), the most common smectites in soils include montmorillonite, beidellite, and nontronite, which may have different formation pathways. These minerals may be inherited directly from the parent material, especially from lithologies such as shales, claystones, and limestones; may result from the transformation of preexisting minerals, such as micas, vermiculites, and mafic chlorites; or may originate by neogenesis from direct precipitation in the soil solution. The occurrence of smectites in soils of the Northeast region of Brazil is strongly associated with dry climatic conditions, in which water limitation restricts advanced weathering and favors the stability of these minerals, indicating arid and semiarid environments (FERREIRA et al., 2016; ARAÚJO FILHO et al., 2017).

In addition, peaks corresponding to 1:1-type clay minerals of the kaolinite group were identified with high intensity in all treatments. The pronounced presence of kaolinite, associated with subordinate iron oxides such as hematite and goethite, mainly in natural clay, and the reduced reflections of these oxides after the K⁺-saturated clay heated to 550 °C and Mg²⁺-saturated clay solvated with ethylene glycol treatments (Figures 2a, 2b, and 2c), indicate a mixed mineral assemblage containing minerals with different degrees of stability and evolution.

Although kaolinite predominance may appear inconsistent with poorly developed soils, this pattern has been widely reported for soils of the Chapada do Apodi. Classic and recent studies (ERNESTO SOBRINHO, 1979; FERREIRA et al., 2016; RÊGO et al., 2016; LOPES et al., 2022) have shown that the significant presence of kaolinite in these environments may be associated with both inheritance from parent material and localized mineral transformation processes influenced by microenvironmental variations, such as drainage and water availability. Therefore, the coexistence of kaolinite and 2:1 minerals indicates the simultaneous occurrence of neoformation, transformation, and mineral preservation processes and the pedogenetic complexity of soils in semiarid environments.



Ve = vermiculite; Il = illite; Mi = mica; Ct = kaolinite; Mt = montmorillonite; Qt = quartz; Gt = goethite; Ht = hematite; Nat = natural clay; MgEg = magnesium-saturated clay sample solvated with ethylene glycol; K550 = potassium-saturated clay sample heated to 550 °C.

Figure 2. X-ray diffraction patterns of the clay fraction of the diagnostic horizons of the soil profiles P1 (A), classified as Luvisolo; P7 (B), classified as Cambissolo; and P13 (C), classified as Vertissolo, evaluated in Mossoró, State of Rio Grande do Norte, Brazil.

The pronounced presence of kaolinite in these soils can be partly explained by mineralogical inheritance from the parent material, especially the occurrence of muscovite in limestone, as well as by the geochemical conditions of the system. In environments with relatively high pH and balanced basic cation contents (K^+ , Ca^{2+} , and Mg^{2+}), greater silica solubilization occurs, favoring the formation of 1:1-type clay minerals, such as kaolinite, even under semiarid conditions, where leaching is limited. In addition, the interpretation of current mineralogy should consider paleoclimatic influence because evidence indicates that the Northeast region of Brazil experienced wetter periods during the Quaternary, with greater chemical weathering intensity and silica removal, favoring kaolinite formation. Therefore, the occurrence of this mineral in relatively slightly weathered soils may reflect both inheritance and previous phases of pedogenetic evolution.

In profile P7 (Cambissolo), the greater intensity of goethite reflections is associated with the higher iron oxide contents (Figure 2b; Table 4). In profile P13, classified as a Vertissolo, the predominance of 2:1 minerals, such as illite, micas, and especially montmorillonite, indicates low leaching and high base saturation, which are characteristic of Vertissolos. The intensity of the reflections of these minerals indicates their predominance in the mineral composition of the clay fraction and the high expansiveness of this soil class (Figure 2c).

In profiles developed from the Barreiras Group (P4 and

P11) and the Detrital-Lateritic Cover (P9, P10, and P12), well-defined kaolinite peaks were observed in the clay fraction of the diagnostic horizons (Figures 3a, 3b, 3c, 3d and 3e). This pattern is consistent with the more weathered nature of these materials, which are frequently associated with soils such as Argissolos, in which desilication and base removal favor the formation and accumulation of 1:1-type clay minerals.

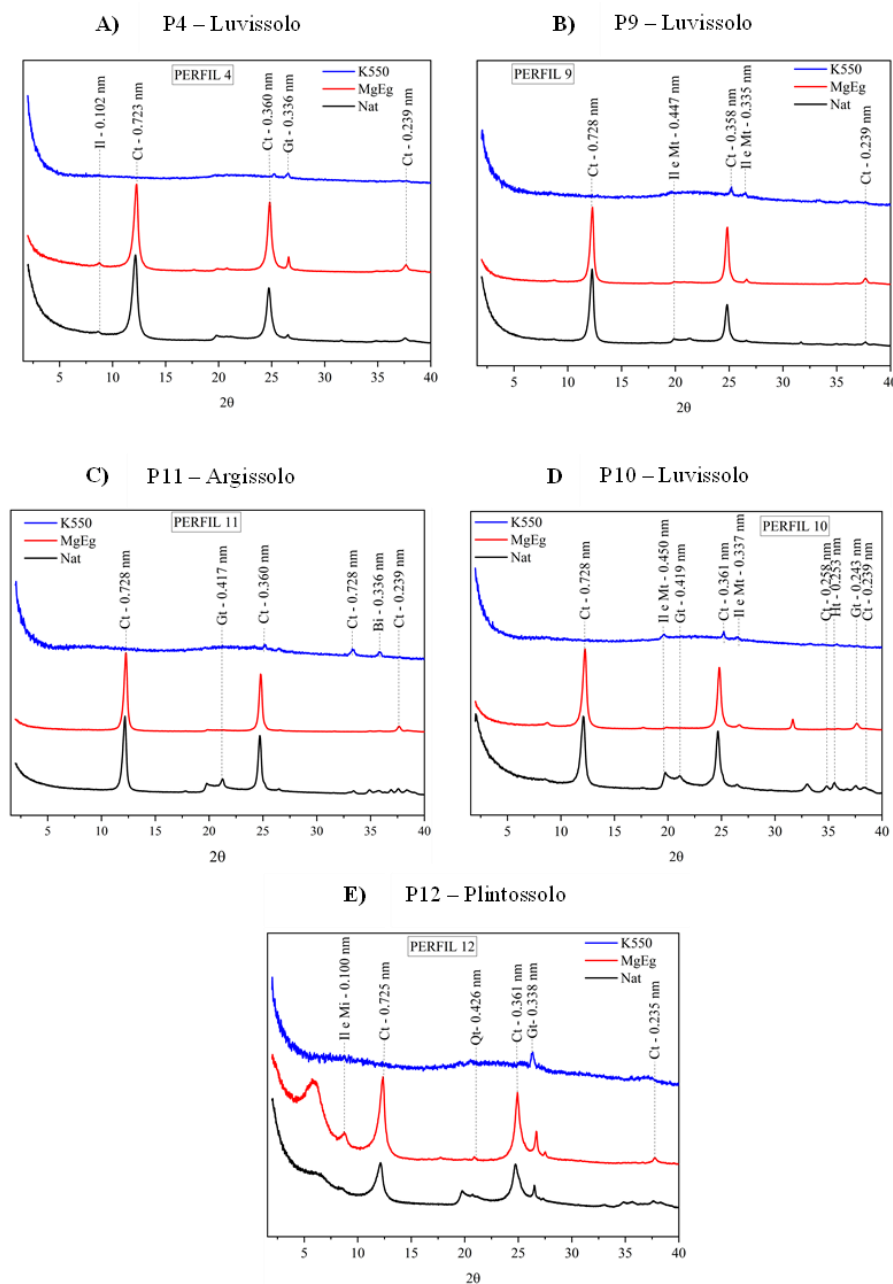
Profiles P4 and P9 (Luvisolos) (Figures 3a and 3b) and P11 (Argissolo) (Figure 3c) had similar mineralogical patterns, characterized by the presence of well-crystallized kaolinite whose reflections persisted after the different treatments, indicating its stability and predominance in the clay fraction. The concomitant presence of illite, a nonexpansive 2:1 clay mineral, indicates contributions from both parent material and mineral transformation processes, possibly related to mica alteration. This coexistence of 1:1 and 2:1 minerals indicates complex pedogenetic systems in which inheritance, transformation, and neoformation occur simultaneously.

In profile P10 (Luvisolo), in addition to well-defined kaolinite peaks, pronounced reflections of iron oxides, particularly goethite and hematite, were identified (Figure 3d). This mineralogical pattern is consistent with the morphological characteristics observed in the profile, such as color and consistency, as well as with the higher Fes and Fed contents shown in Table 4, indicating a greater concentration of more stable iron forms.

Well-defined kaolinite peaks were also observed in P12 (Plintossolo), with significant reduction or disappearance after K saturation followed by heating to 550 °C, a response consistent with the identification of this clay mineral. In addition, reflections of goethite, quartz, mica, and illite were identified with lower relative intensity, indicating the secondary contribution of these minerals to the composition of the clay fraction (Figure 3e). This mineral assemblage indicates contributions from both parent material and

differentiated pedogenetic processes, including possible water-regime oscillations typical of environments associated with Plintossolos.

Overall, iron oxides were identified in almost all profiles, with predominance of hematite and goethite. The distribution and intensity of the reflections of these minerals indicate variations in degree of crystallinity and formation conditions, as well as local differences in the pedogenetic environment.



Il = illite; Ct = kaolinite; Gt = goethite; Mt = montmorillonite; Bi = biotite; Ht = hematite; Mi = mica; Nat = natural clay; MgEg = magnesium-saturated clay sample solvated with ethylene glycol; K550 = potassium-saturated clay sample heated to 550 °C.

Figure 3. X-ray diffraction patterns of the clay fraction of the diagnostic horizons of P4 (A), P9 (B), and P10 (D), classified as Luvisolos; P11 (C), classified as Argissolo; and P12 (E), classified as Plintossolo, evaluated in Mossoró, State of Rio Grande do Norte, Brazil.

Comparison of the results obtained with those described in the V RCC (EMBRAPA, 1998) shows similarity in the mineralogical composition of the clay fraction of the studied soils, especially the combined presence of kaolinite, 2:1 minerals, and iron oxides. However, soils subjected to more intense pedogenetic processes show greater kaolinite predominance, whereas less weathered soils retain a greater proportion of 2:1-type clay minerals, such as micas, illites, and smectites. Araújo Filho et al. (2017) emphasized that, because of the diversity of parent materials and the environmental conditions of the Semiarid region of Brazil, variable proportions of clay minerals are common and indicate the complexity of the pedological systems of this region.

The results of this study indicate that the mineralogical composition of the clay fraction and the distribution of iron forms are controlled by the interaction between parent material and weathering intensity. Soils developed from the Jandaíra Formation have a predominance of 2:1-type clay minerals, especially smectites, favored by high base saturation and low leaching intensity under semiarid conditions. In these soils, iron contents indicate the predominance of structural forms and lower iron removal during pedogenetic evolution.

In contrast, soils derived from the Barreiras Group and Detrital-Lateritic Cover have mineralogy dominated by 1:1-type clay minerals, especially kaolinite, and a greater proportion of more stable iron oxides, such as goethite and hematite, indicating a higher degree of weathering and desilication. The Alluvial Deposits have greater mineralogical variability because of the heterogeneity of transported sediments, resulting in the coexistence of slightly weathered primary minerals, 2:1 clay minerals, and iron forms with different degrees of crystallinity.

Therefore, the results indicate that the composition of the clay fraction and the distribution of iron forms are controlled by the interaction among parent material, physical and chemical attributes, and degree of weathering. Less developed soils showed greater influence of parent material, whereas more developed soils, with lower cation exchange capacity, lower base saturation, and sandier texture, showed greater leaching and lower iron contents. The presence of kaolinite, smectites, and iron oxides is an important indicator of the genesis and evolution of semiarid soils and provides support for fertility management and the definition of sustainable use strategies, considering the limitations and potential of these environments.

CONCLUSIONS

The soils of Mossoró, Rio Grande do Norte, Brazil, have mineralogical and pedogenetic diversity, with predominance of a hypoferric to mesoferric character and crystalline iron forms. Cambissolos and Neossolos generally had high iron contents, although high values were also observed in profiles classified as Luvisolos and Vertissolos, indicating the strong influence of parent material.

Soils derived from carbonate materials have a greater occurrence of 2:1 clay minerals and greater participation of structural iron, whereas those formed from more weathered sandy sediments are dominated by kaolinite and more crystalline iron oxides. This pattern indicates that more developed soils in the Semiarid region of Brazil, such as

Argissolos, Plintossolos, and Luvisolos, are dominated by kaolinite and iron oxides, whereas less developed soils, such as Neossolos, Vertissolos, and Cambissolos, are characterized by the predominance of 2:1 clay minerals, reflecting the combined control of parent material and degree of weathering on the mineralogy of the clay fraction.

The results indicate that parent material and degree of weathering control the mineralogy and iron forms in the studied soils, with implications for natural fertility potential, nutrient replacement, and organic matter conservation, which are fundamental aspects for the sustainable use of soils in semiarid environments.

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