Ciência e Agrotecnologia
SCIENCE AND AGROTECHNOLOGY

Ciência e Agrotecnologia, 45:e018121, 2021
http://dx.doi.org/10.1590/1413-7054202145018121

Agricultural Sciences
eISSN 1981-1829

Study of an abnormal occurrence of Oxisols in strongly undulated relief in the south of Minas Gerais, Brazil, with support of pXRF and geomorphology

Estudo da ocorrência rara de Latossolos em relevo forte ondulado no sul de Minas Gerais, Brasil, com apoio de pXRF e geomorfologia

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Received in August 20, 2021 and approved in October 15, 2021

ABSTRACT

Oxisols are the main soils in Brazil and they classically occur in stable and gentle geomorphic surfaces. However, in the south of Minas Gerais State, Oxisols have been observed under strongly undulated relief, a very rare condition for these soils in this physiographic region. Therefore, this work aimed to assess the elemental dynamics and relief enhanced with portable X-ray fluorescence (pXRF) spectrometry, associated to geomorphology, to understand such occurrence. The studied soils are located in Muzambinho municipality, Minas Gerais State, Brazil. Oxisol profiles were characterized in the upper third (P1), middle third (P2) and lower third (P3) of the hillslope. After morphological description, soil samples were collected in the A, AB and Bo horizons of the profiles. Physical, chemical and pXRF analyses of the soils were carried out in the laboratory. Ti and Fe content (pXRF) had a high correlation with the soil textural fractions. High weathering-leaching degrees were determined, although they occur on a steep slope where younger soils (Inceptisols) would be expected in this region. The altitudinal concordance of summits observed in the more elevated surrounding areas indicates a flat paleorelief, helping to explain this unusual occurrence. The soils' weathering degree values decreased down the hillslope, indicating silica enrichment through runoff and subsuperficial water flux in the lower landscape positions. The pXRF analyses assisted the characterization of these old soils occurring in steep relief. It provided bases for confirming their high weathering degree indexes and detected evidences of the pre-weathering of the regolith of this very old landscape.

Index terms: Steep slopes; proximal sensors; tropical soils; weathering.

RESUMO

Latossolos são os principais solos do Brasil e classicamente ocorrem em superfícies geomórficas suavizadas e estáveis. No entanto, no Sul de Minas Gerais, Latossolos têm sido observados em relevo forte ondulado, uma condição rara para estes solos nesta região fisiográfica. Este trabalho teve como objetivo acessar a dinâmica elementar e o relevo com uso de espectrometria de fluorescência de raios-X portátil (pXRF), em associação à geomorfologia, para entender tal ocorrência. Os solos estudados estão localizados no município de Muzambinho, Estado de Minas Gerais, Brasil. Perfis de Latossolo foram caracterizados no terço superior (P1), terço médio (P2) e terço inferior (P3) da encosta. Após a descrição morfológica, amostras de solo foram coletadas nos horizontes A, AB e Bw dos perfis. Foram realizadas análises físicas, químicas e espectrométricas dos solos em laboratório. Os teores de Ti e Fe (pXRF) tiveram alta correlação com as frações texturais dos solos. Foram encontrados altos graus de intemperismo-lixiviação dos Latossolos, embora ocorram em encosta íngreme onde solos mais jovens (Cambissolos) seriam esperados. A concordância de altitude dos topos observada nas áreas circundantes mais elevadas indica um paleorrelevo plano, ajudando a explicar esta ocorrência anormal. Os valores dos índices de intemperismo dos solos diminuíram ao longo da encosta, indicando o enriquecimento de sílica por escoamento superficial e fluxo de água subsuperficial nas posições mais baixas da paisagem. As análises de pXRF ajudaram na caracterização destes solos velhos em topografia forte ondulada. O equipamento forneceu bases para confirmação dos seus altos graus de intemperismo, além de detectar evidências do pré-intemperismo do regolito dessa paisagem muito antiga.

Termos para indexação: Encostas íngremes; sensores próximos; solos tropicais, intemperismo.

2021 | Lavras | Editora UFLA | www.editora.ufla.br | www.scielo.br/cagro
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INTRODUCTION

Latosols (Santos et al., 2018), Oxisols (Soil Survey Staff, 2014) or Ferralsols (Food and Agriculture Organization - FAO, 2014) are the most important and widely distributed soils in Brazil. In general, Brazilian Oxisols are highly weathered-leached, which causes the residual accumulation of Fe, Al and Ti oxide minerals, and removal of silica and bases, acidifying these soils (Ker, 1998). They commonly have as advantages the microgranular structure in the Bo horizon, good drainage, high effective depth, and adequate balance of macro- and micropores for root system growth and crop development.

A relevant factor for Oxisols formation is the relief (Jenny, 1941), generally occurring under slopes ranging from flat to gently undulated (Resende et al., 2014, 2021). The relief conditions soil formation by affecting the water flow and the transportation of soil constituents (Campos et al., 2012; Canellas et al., 2000). Accordingly, it is a paramount factor driving soil differentiation across the landscape (Kämpf; Curi, 2012).

However, some Oxisols are found in steep slopes, an atypical condition for their occurrence. Presumably, since Oxisols are intensely weathered and deep, they should need a smoother surface to fully develop, where pedogenetic processes are more intense than erosion, otherwise they would remain as young soils and never develop enough to be classified as Oxisols. Thus, the reasons behind their occurrence in strongly undulated relief are not completely understood by soil scientists.

The development of these soils under a paleorelief can explain this occurrence. These soils may have formed when landforms were very different from the modern age, when the region was flatter, followed by a later dissection of the landscape, but still maintaining their classification as Oxisols (Resende et al., 2014; Rezende et al., 2021), unless the thickness of Bo horizon is less than 50 cm, framing them alternatively as Inceptisols, which is not the situation in this study. The investigation of such cases can enrich the literature and complement the current knowledge about soil formation. Novel technologies might be able to aid this endeavor, such as the portable X-ray fluorescence (pXRF).

The pXRF provides the total elemental content of samples and has been successfully employed in many soil studies (Silva et al., 2021; Weindorf; Bakr; Zhu, 2014). It has been adopted for the study of several soil properties, such as texture (Zhu; Weindorf; Zhang, 2011), soil nutritional analysis (Lima et al., 2019; Pelegrino et al., 2021), soil biology (Teixeira et al., 2021), soil mapping (Mancini et al., 2019; Silva et al., 2016), soil genesis and classification (Gozukara; Zhang; Hartemink, 2021; Silva et al., 2018, 2021; Stockmann et al., 2016; Sun et al., 2020), characterization of different land uses (Chakraborty et al., 2019), soil salinity (Swanhart et al., 2014), soil contamination (Horta et al., 2021; Kebonye, 2021), among others, showing up as a useful tool for such studies.

Seemingly, it could be applied for soil weathering studies. As soils develop, some oxides residually accumulate, such as Al_2O_3, Fe_2O_3, TiO_2. Weathering indexes relate these oxides with silica (SiO_2), which is leached during soil formation, attempting to measure the degree of weathering (Santos et al., 2018). The usual approach is to calculate the silica/alumina or the silica/(alumina+Fe_2O_3) ratios (Zhang, Hartemink, 2019); but alternatively, one can relate all mentioned oxides, as proposed by Singh, Parkash and Singhvi (1998). The oxides needed for these indexes are commonly obtained by laboratory analysis, but sensors like pXRF are able to provide such data and simplify the methodology.

Thus, this work aimed to assess the aspects of elemental dynamics, weathering and geomorphology of old soils observed under unusual steep relief enhanced by pXRF spectrometry to understand such abnormality. The hypothesis is that the chemical characterization provided by pXRF and its association with geomorphology will improve our knowledge about tropical soils formation. Although in tropical conditions the use of pXRF has increased, without generation of chemical waste (“green analyses”) (Silva et al., 2021), this approach was not yet applied to investigate and characterize Oxisols that occur in steep relief. The low-cost and agile methods enabled by pXRF could allow for quick and effective analyses, providing important insights regarding the formation of such soils.

MATERIAL AND METHODS

Study area, soil profiles description and sampling

The study area is located at the Atlantic Forest biome, in the Instituto Federal de Educação, Ciência e Tecnologia do Sul de Minas Gerais (IFSULDEMINAS), in the Muzambinho municipality, south of Minas Gerais State, Brazil. In the IFSULDEMINAS *campus*, Oxisols represent 53% of the total area; from them, 11% are located in slopes steeper than 20% (Batista; Santos, 2017). The parent material of these Oxisols is gneiss (Table 1). According to Köppen’s classification, the climate in this region is Cwb (temperate humid climate, with dry winters and rainy summers). The mean annual temperature is 18 °C and the mean annual rainfall is 1,605 mm (Alvares et al., 2013; Aparecido et al., 2014). The main native vegetation is represented by the semiperennial tropical forest.

Table 1: Example of the chemical composition of gneiss fragments obtained via pXRF in Lavras, Minas Gerais, Brazil. Adapted from Mancini et al. (2019).

Gneiss chemical composition	
Total elemental content (%)	
Al	15.037
Ca	0.665
Fe	0.713
K	0.563
Mg	1.301
Mn	0.001
P	0.038
Si	35.317
Ti	0.127

Soil profiles were morphologically described and sampled on a strongly undulated relief under a planted pasture area (Figure 1). Profile 1 (P1) is located in the upper third of the hillslope, coordinates 21º21'06'' S and 46º31'41''W; profile 2 (P2), in the middle third of the hillslope, coordinates 21º21'07'' S and 46º31'40'' W; and profile 3 (P3), in the lower third of the hillslope, coordinates 21º21'09'' S and 46º31'39'' W. The slope on these soil profiles is shown in Figure 1. The altitude ranged from 945 m in P3 to 1,025 m in P1 (Figure 1). The horizontal distance from P1 to P2 is 42 m, and from P2 to P3, 75 m. The slope on each point is: P1 – 18.3%, P2 – 25.7%, P3 – 29.2%. The soils were classified as Latossolo Vermelho-Amarelo distrófico típico (P1 and P2) and Latossolo Amarelo distrófico típico (P3) (Santos et al., 2018), corresponding to Typic Hapludox (P1 and P2) and Xanthic Hapludox (P3), according to US Soil Taxonomy (Soil Survey Staff, 2014), and to Haplic Ferralsol (P1 and P2) and Xanthic Ferralsol (P3), according to the Word Reference Base (FAO, 2014). The different classification systems were presented for reference, but studied soils will be addressed using the US Soil Taxonomy throughout the text for consistency.

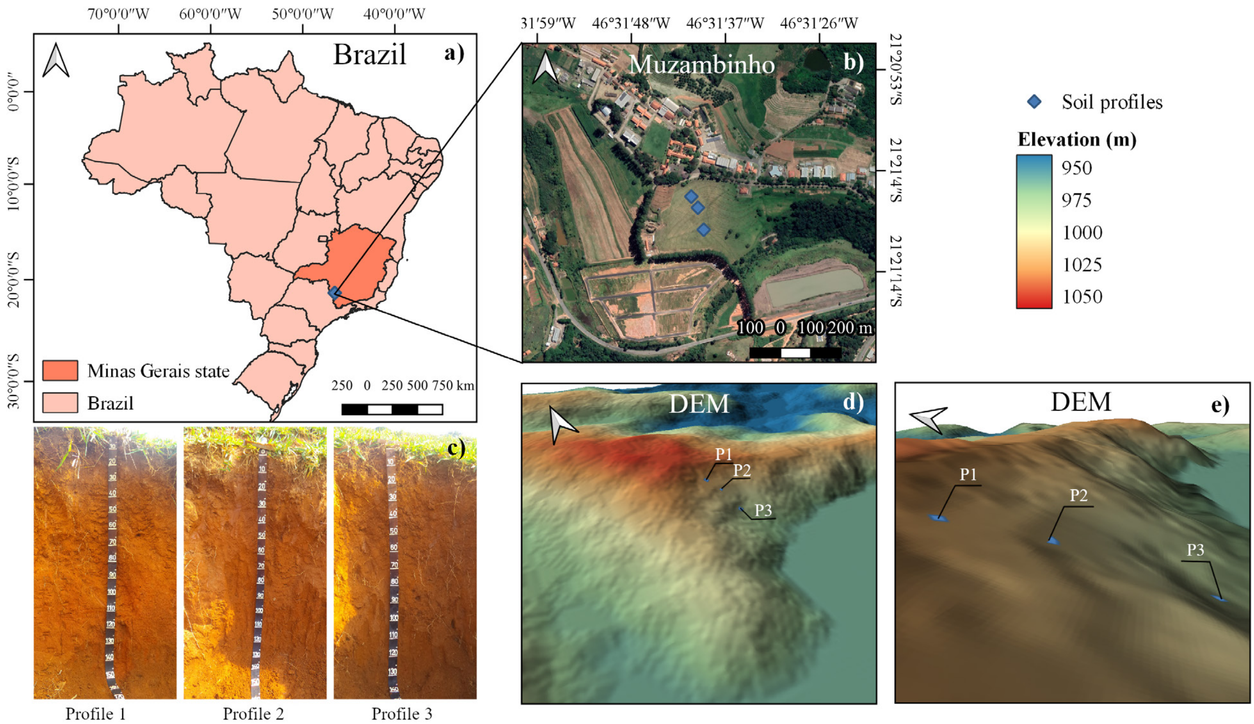

Figure 1: Location of the study area (a and b), studied soil profiles (c) and the respective digital elevation model (d and e). The area is located in the Muzambinho municipality, south of Minas Gerais State, Brazil. P1: Profile 1; P2: Profile 2; P3: Profile 3, DEM: Digital elevation model.

Profile morphological description was conducted as suggested by Santos et al. (2015). Composite samples of the A, AB, and Bo horizons were collected to perform the chemical, physical and pXRF analyses.

Soil texture and fertility analyses

The collected samples were air-dried and sieved (2 mm) (air-dried fine earth -ADFE) for the chemical and texture analyses. The pH was obtained in water (soil:water ratio of 1:2.5) (Donagema et al., 2011). Exchangeable contents of Ca^{2+}, Mg^{2+}, and Al^{3+} were obtained by extraction with 1 mol L^{-1} KCl (Mclean et al., 1958). Available contents of K^{+} and P were obtained by extraction utilizing Mehlich-1 solution (Mehlich, 1953); H^{+}+Al^{3+} were determined by the SMP extractor (Shoemaker; Mclean; Pratt, 1961). The available B was determined using hot water as proposed by Berger and Truog (1939) and the available Cu, Zn, Mn, and Fe were extracted with Mehlich-1 solution and measured through the atomic absorption spectrometry (Mehlich, 1953).

Soil organic matter (SOM) content was determined according to Walkley and Black (1934). Cation exchange capacity (CEC) was calculated by the sum of Ca^{2+}, Mg^{2+}, K^{+}, Al^{3+} and H^{+} contents. Particle size distribution analysis was performed by the pipette method according to Gee and Bauder (1986).

Analyses via pXRF spectrometry

The pXRF analyses of ADFE samples were conducted on a DP-600 (Olympus Waltham, MA) spectrometer, during 60 seconds, operating in Soil Mode (Silva et al., 2021; Weindorf; Chakraborty, 2016). To ensure the efficiency of this proximal sensor, two soil materials certified by the National Institute of Standards and Technology (NIST), 2710a, and 2711a, and a material provided by the pXRF manufacturer (check sample) were analyzed by pXRF and the obtained contents were compared with the certified values.

Five elements were used in this study due to their importance as soil weathering indicators (Ker; Novais, 2011; Resende et al., 2019): Ti, Mn, Si, Al and Fe. All the recovery values of these elements (content yielded by pXRF/certified content x 100) were higher than 70%. From these results, indexes traditionally used in the literature, as cited below (Equations 1, 2 and 3), were applied to assess soil weathering. The following soil weathering indexes were calculated using oxide total values obtained by pXRF:

$$\text{Di} = \frac{\text{SiO}_2}{\left(Al_2O_3 + Fe_2O_3 + TiO_2\right)} \quad (1)$$

(Singh; Parkash; Singhvi, 1998)

$$\text{Ri} = \frac{\text{SiO}_2}{Al_2O_3} \quad (2)$$

(Ruxton, 1968)

$$\text{Zi} = \frac{\text{SiO}_2}{\left(Al_2O_3 + Fe_2O_3\right)} \quad (3)$$

(Zhang, Hartemink, 2019)

Statistical analyses and geographic information

Pearson's correlation between the elements obtained by pXRF analyses and both texture and soil fertility results were calculated with the aid of the R software (R Core Team, 2021), using the package *corrplot* (Wei; Simko, 2021) that also calculated the significance of the results. A digital elevation map for the region was applied to analyze the morphology of the landscapes and it was obtained from the Alaska Satellite Facility Distributed Active Archive Data Center (ASF DAAC), with a resolution of 12.5 m. The elevation data was used to visualize cross sections cutting through the studied area's relief, in order to examine the hilltop altitudes surrounding the region. This analysis was performed via the software QGIS (version 3.12.3).

RESULTS AND DISCUSSION

Morphological, physical and fertility properties of the soil profiles

The soil structure found in the three profiles was granular in the A horizon, and microgranular in the Bo horizon. In all the analyzed profiles, roots were observed in depth, which indicates adequate porosity for soil aeration and good drainage, attributes compatible with clayey Oxisols with such structure. Table 2 shows the main morphological attributes identified in the three soil profiles.

Profiles 1 and 2 presented dominant red-yellow color, while profile 3 presented yellow color in the Bo horizon (Table 2). There are several aspects to be considered in pedogenic studies that influence soil color, such as soil mineralogy, drainage class, soil water regime, soil organic matter (SOM), past and current climate, among others (Ibáñez-Asensio et al., 2013; Ker et al., 2012; Lepsch, 2010; Resende et al., 2011). In this context, the iron oxide minerals have remarkable importance. The clay fraction of soil profiles 1 and 2 have both hematite and goethite, while profile 3 presents only goethite (data not shown), which is in accordance with their colors.

In the P1 and P2 profiles, the hue in the superficial horizons is brown, but not below. In the P3 profile, all the horizons are brown, reflecting a subtle hydrosequence of soils conditioned by the relief (Curi; Franzmeier, 1984). Down the slope, soils get closer to the parent material, hence drainage is reduced and the tendency of accumulation of SOM increases, darkening the horizon – notice the chroma/value of 4/4 in P3 below 27 cm, lower than other profiles in the same depth.

Slight texture variations were observed among the soil profiles (Figure 2). The texture of the soil profiles varied between clayey and very clayey, indicating the high degree of weathering of these soils (Resende et al., 2019), derived from gneiss.

Table 2: Soil classes, horizons, depth, Munsell color, and structure of the three profiles located at the IFSULDEMINAS, Muzambinho municipality, Minas Gerais state, southeastern Brazil.

Profile	Soil (US[1])	Soil (WRB[2])	Soil (SiBCS[3])	Horizon	Depth (cm)	Moist color	Structure
1	Typic Hapludox	Haplic Ferralsol	Latossolo Vermelho-Amarelo distrófico típico	A	0-20	Dark reddish brown (5YR 3/3)	Granular
				AB	20-27	Reddish brown (5YR 5/4)	Granular
				Bo	27-300+	Yellowish red (5YR 5/6)	Microgranular
2	Typic Hapludox	Haplic Ferralsol	Latossolo Vermelho-Amarelo distrófico típico	A	0-13	Reddish brown (5YR 4/3)	Granular
				AB	13-27	Reddish brown (5YR 4/4)	Granular
				Bo	27-300+	Yellowish red (5YR 5/7)	Microgranular
3	Xanthic Hapludox	Xanthic Ferralsol	Latossolo Amarelo distrófico típico	A	0-20	Dark brown (7.5YR 3/3)	Granular
				AB	20-27	Strong brown (7.5YR 5/6)	Granular
				Bo	27-300+	Brown (7.5YR 4/4)	Microgranular

[1]US Soil Taxonomy (Soil Survey Staff, 2014); [2]World Reference Base (FAO, 2014); [3]Brazilian Soil Classification System (Santos et al., 2018).

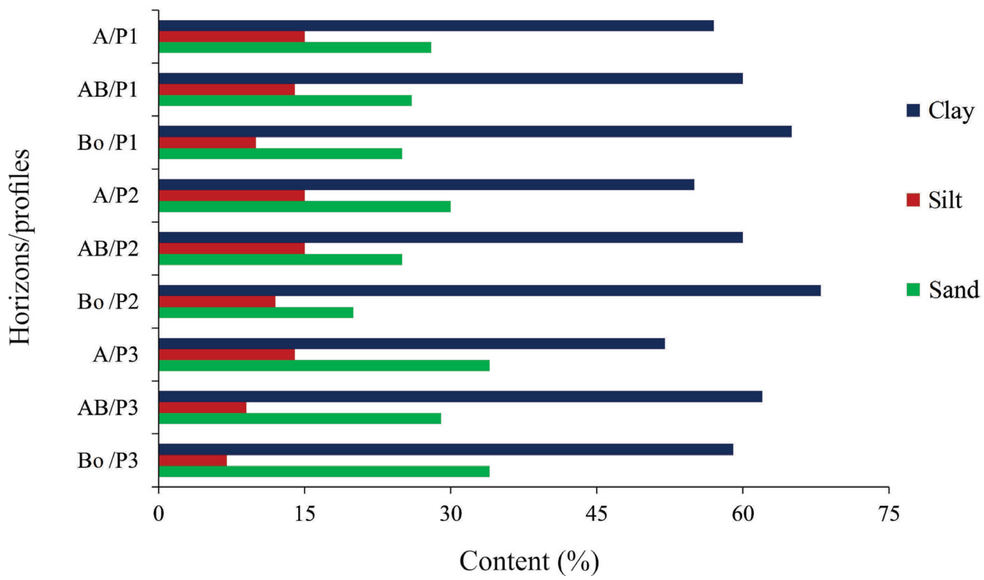

Figure 2: Particle size distribution of the soil profiles horizons located at the IFSULDEMINAS, Muzambinho municipality, Minas Gerais State, southeastern Brazil.

Soil fertility analyses (Table 3) showed that the superficial horizons of three profiles had pH values higher than commonly found in Oxisols under natural conditions, which tend to be more acidic (Lopes; Guilherme, 2016). These high pH values along with the Ca^{2+} contents in the superficial horizons indicate that these planted pasture areas have received limestone.

Both SOM and CEC decrease with depth. The mutual decrease of both variables shows how these weathered soils depend on SOM to retain cations, reinforcing the importance of SOM on the generation of negative superficial charges for retaining bases in these low-activity clay soils. SOM increases down the slope in Bo, being highest in P3. This indicates a slight poorer drainage in P3 helping to preserve SOM. These soils contain kaolinite, gibbsite, hematite (except in profile 3) and goethite in the clay fraction which have very low CEC. Fe and Al mineral oxides, such as hematite, goethite and gibbsite at pH values below 7.0 tend to present anion exchange capacity (AEC) greater than CEC (Fageria, 2012). Conversely, in soils with such pH values SOM and kaolinite generate negative superficial charges, thus contributing to the increase of CEC (Franks et al., 2021; Inda Junior et al., 2017).

The base saturation (BS) values, except for the superficial horizons, are low, as expected for Oxisols. In the A horizon, the liming application helps to explain the higher values. The low aluminum saturation (AS) values are related to Al constant consumption for gibbsite formation (Curi; Franzmeier, 1984) in addition to liming application in the superficial horizons.

Soil total element contents obtained by pXRF

Figure 3 presents the pXRF results for Al, Si, Fe, Ti and Mn. In P1 and P2, there was a high content of Al in comparison to Si (Figure 3a), evidencing the high weathering degree in these soil profiles. During the weathering process, easily-weatherable primary minerals (EWPM) suffer hydrolysis and hence can form kaolinite and iron and aluminum oxides (Inda Junior et al., 2017; Kämpf; Curi, 2003; Kämpf; Curi; Marques, 2009). Campos et al. (2012) studied the soil-landscape relationships and verified that the formation, persistence and elemental contents of clay minerals were mainly conditioned by relief. However, the mineralogy of soils herein does not match their landscape position: more primary minerals are expected in soils formed under steep slopes, instead of oxide-rich old soils with low Si content.

Compared to P1 and P2, P3 showed an increment in the Si content (Figure 3a), evidencing a relative decrease in the soil weathering degree, associated with a longer water residence time, conditioned by relief (lower third of the landscape) through silica addition from runoff and subsuperficial water flux (Moniz; Buol, 1982). In this study, where soils are derived from gneiss, differential Si contents among the profiles may indicate their differential weathering degrees driven mainly by relief conditions (Figures 3a and 3b).

Different patterns of Al and Fe across horizons for each profile probably reflect the variation of parent material chemical traits (Figure 3a). P3 had a higher Si content compared with Al and Fe. Silva et al. (2020) found lower contents of Fe_2O_3 and TiO_2 and greater contents of SiO_2 in soils derived from gneiss compared to soils developed from itabirite, basalt, gabbro and tuffite.

Table 3: Fertility analyses of Oxisol profiles located at the IFSULDEMINAS, Muzambinho municipality, Minas Gerais state, southeastern Brazil.

Soil	Hor.	pH	H+Al	Al^{3+}	CEC	SOM	P	K^+	Ca^{2+}	Mg^{2+}	BS	AS	Fe	Mn	Zn	Cu	B
			-----$cmol_c$ dm^{-3}-----			dag kg^{-1}	mg dm^{-3}		$cmol_c$ dm^{-3}		----%----		--------------mg dm^{-3}--------------				
P1	A	6.54	3.38	0.15	5.5	2.48	0.6	26	1.95	0.11	38.67	6.59	82.4	8.9	0.9	2.3	0.16
	AB	5.63	3.38	0.28	4	1.64	0.6	15	0.5	0.04	14.46	32.62	42.8	3.4	0.2	2.3	0.18
	Bo	5.59	2.29	0.06	2.4	0.54	0.2	0	0.1	0.02	5.00	33.33	18.6	1.4	0.2	1.7	0.11
P2	A	6.98	1.65	0	7.9	3	1.2	29	4.46	1.77	79.80	0	57.3	19.6	1.1	1.8	0.18
	AB	6.81	1.84	0	4.6	1.52	0.6	9	2.36	0.4	60.50	0	27.3	4	0.2	2.1	0.2
	Bo	5.74	2	0	2.4	0.86	0.2	4	0.37	0.02	16.68	0	21	1.5	0.2	1.5	0.15
P3	A	6.69	3.08	0.18	4.8	2.36	0.9	32	1.32	0.31	35.67	9.51	74.6	14.6	0.6	2.1	0.2
	AB	5.6	3.08	0.41	3.3	1.18	0.2	8	0.22	0.02	7.89	61.15	32	3.8	0.2	1.7	0.16
	Bo	5.52	3.56	0.37	3.7	0.97	2.1	0	0.13	0.02	4.05	71.15	34.5	5.3	0.2	1.4	0.15

CEC: Cation exchange capacity; SOM: Soil organic matter; BS: Base saturation; AS: Aluminum saturation.

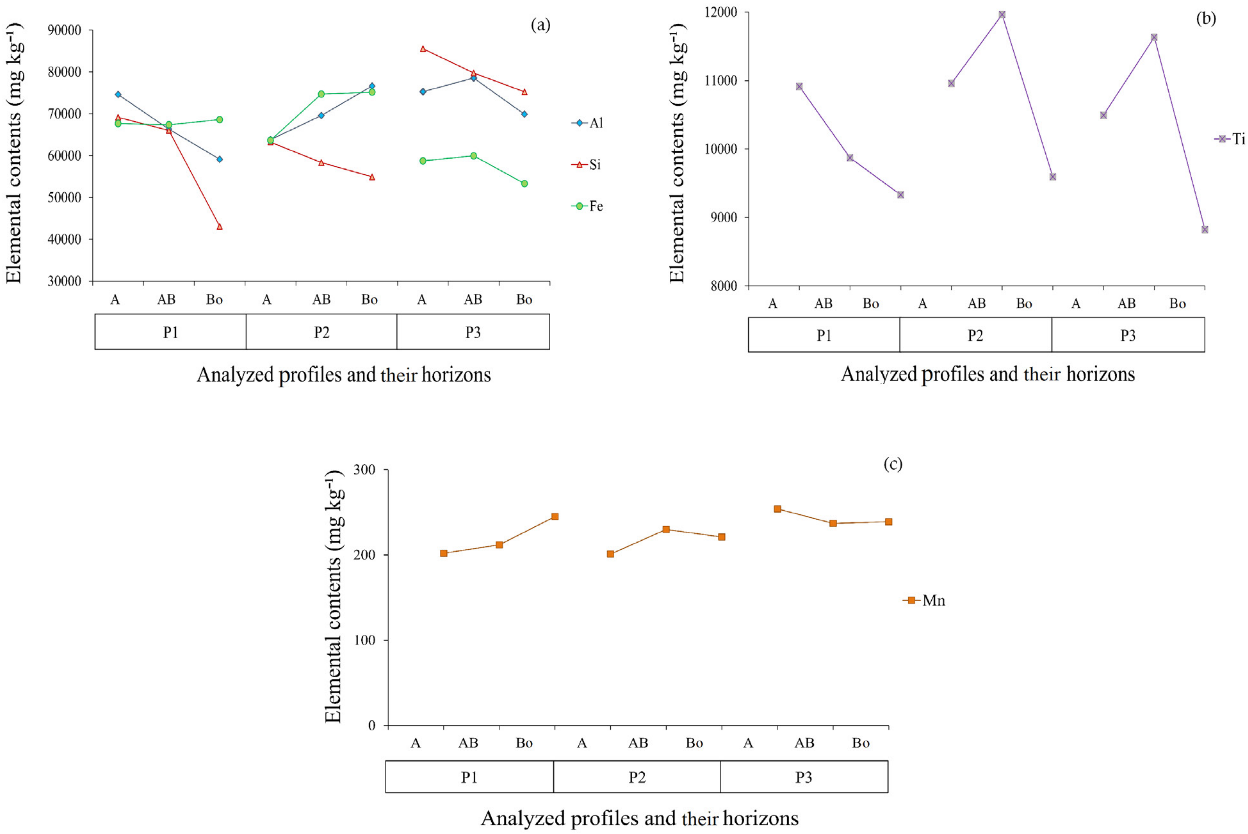

Figure 3: Elemental contents obtained by pXRF in the studied horizons of Oxisol profiles located at the IFSULDEMINAS, Muzambinho municipality, Minas Gerais state, southeastern Brazil.

The Fe content varied less in the soils in upper and middle third of the landscape (P1=68,596; P2=75,160 mg kg^{-1}; values for Bo horizon), while in the lower third there was a drastic reduction (P3=53,297 mg kg^{-1}; Bo horizon). During fieldwork, it was observed that the hues were redder in P1 and P2 and yellower in P3. In the lower third of the landscape, where more water tends to accumulate, in addition to the lower Fe content, the formation of goethite over hematite is favored, making this soil yellower than the others (Figure 3a). Table 3 shows more available Fe content in the Bo horizon of P3, which is possibly due to a greater moisture degree, favoring some seasonal reduction of Fe(III) and consequent increase of Fe(II) compounds (Resende et al., 2021; Kämpf; Curi, 2012; Schwertmann; Taylor, 1989). There is no certainty as to why the drainage regime is different in P3, but all mentioned evidences showed that it is distinct from P1 and P2. The main hypotheses for this phenomenon are the proximity to the parent material (and thus the water table), and the retention of water due to the higher SOM content.

Values of silica/alumina ratio for Bo horizons were 0.83 in P1, 0.81 in P2, and 1.22 in P3 (Table 4). The other indexes show a similar behavior, indicating higher weathering degree in the Bo horizon (except for P3), which was completely unexpected. This trend can be observed in all three studied soil profiles (Table 4) and indicates a pre-weathering of these soils, facilitated by the mafic lamellae of the gneiss (Mancini et al., 2021), probably in a flatter paleorelief, in accordance with the geomorphology (section 3.4).

According to the weathering degree indexes (Equations 1, 2 and 3), in P3 the weathering is less intense than in P1 and P2, corroborating the aforementioned discussions. Overall, the studied profiles tend to be less weathered down the slope. The decreasing weathering degree order was: P1 $\geq$ P2 > P3 (Table 4). Additionally, P1 and P2 show increasing weathering degree from A to Bo, whilst in P3 the AB horizon is more weathered than Bo. This trend is likely an indication that soils are getting closer to the parent material and/or are less weathered due to poorer drainage compared to P1 and P2. This trend agrees with previously mentioned observations. For instance, soils gradually become yellower down the slope, indicating poorer drainage, which favors the formation of goethite (yellow) over hematite (red) (Table 2); and SOM increases down the slope, evidence of a decrease in drainage efficiency (Table 3).

Table 4: Weathering degree indexes for the studied Oxisol profiles, situated in Muzambinho municipality, Minas Gerais state, Brazil.

Soil	Horizon	Di[1]	Ri[2]	Zi[3]
P1	A	0.67	1.05	0.71
	AB	0.69	1.13	0.73
	Bo	0.48	0.83	0.51
P2	A	0.70	1.12	0.73
	AB	0.57	0.95	0.61
	Bo	0.51	0.81	0.53
P3	A	0.87	1.29	0.91
	AB	0.78	1.15	0.82
	Bo	0.83	1.22	0.87

[1] $Di = \frac{SiO_2}{(Al_2O_3 + Fe_2O_3 + TiO_2)}$ (Singh; Parkash; Singhvi, 1998);

[2] $Ri = \frac{SiO_2}{Al_2O_3}$ (Ruxton, 1968);

[3] $Zi = \frac{SiO_2}{(Al_2O_3 + Fe_2O_3)}$ (Zhang, Hartemink, 2019).

The Al behavior was different in each soil profile (Figure 3a). Aluminum has high concentration in old soils as a residual element, mainly associated with gibbsite and kaolinite in the clay fraction, and in micas, mainly muscovite, in the sand fraction (Brinatti et al., 2010). The Al random distribution in these soils, assessed by pXRF, is probably related to the alternating felsic and mafic laminae of the gneiss, as observed by Mancini et al. (2021) in this region.

In Figure 3b, we can see that Ti contents have a maximum value of 12,000 mg kg^{-1}. Titanium is a less mobile element in soils, being frequently used as a fingerprint of soil parent material (Mancini et al., 2021), and these Oxisols derived from gneiss have lower contents compared to other Oxisols derived from mafic rocks (Ker; Novais, 2011). The Ti oxide minerals frequently found in soils, such as ilmenite ($FeTiO_3$) and anatase (TiO_2), are originated from the weathering of silicates like biotite, hornblende, and augite; Ti can also be found as isomorphous substituent of Fe and Al in the crystalline structure of oxide minerals (Andrade et al., 2009; Araujo et al., 2014).

Mn (Figure 3c) showed little variation across the soil profiles. It was observed a little enrichment with depth in P1 and P2 compared with the Mn superficial quantity: A horizon (P1=202; P2=212 mg kg^{-1}) and Bo (P1=254; P2=237 mg kg^{-1}). This element has a large abundance in the terrestrial crust; there is a great diversity of Mn-bearing minerals in soils and parent materials, such as plagioclases, olivines, pyroxenes, amphiboles and biotites (Andrade et al., 2009). Mn differences between profiles observed herein (Figure 3c) can be explained by the accessory minerals in parent material composition.

Correlations between texture, fertility attributes and pXRF data

The correlation between total Fe and Ti contents (pXRF) with the sand fraction content was high and negative (-0.92 and -0.87, respectively), probably due to the fact the dominant minerals in this soil fraction of Oxisols are quartz and muscovite (Figure 4a), which do not contain such elements in their crystalline structure. Conversely, clay (0.53 and 0.48) and silt (0.52 and 0.54, respectively) fractions had a positive correlation with these elements contents, due to the presence of hematite (Fe_2O_3), maghemite (Fe_2O_3), goethite (FeOOH), ilmenite ($FeTiO_3$), rutile (TiO_2) and anatase (TiO_2) in these soil fractions of Oxisols. Iron is usually strongly correlated to soil texture (Figure 4a), mainly to the clay fraction, which was also observed by O'Rourke et al. (2016).

A strong and positive correlation (0.98; $p<0.05$) between Fe and Ti total contents was observed, which is explained by their similar behavior, residually accumulating in Oxisol profiles (Figure 4a). For Al, Mn and Si contents, weak correlations were found to any textural fraction, probably because they occur in minerals of multiple particle size fractions. For instance, Al may be present in the muscovite crystalline structure in the sand (more common) and silt (less common) fractions, as well as in kaolinite, gibbsite and Fe oxide minerals in the silt and clay fractions of Oxisols. Mn may be an isomorphous substituent of Fe in the oxide minerals in the latter soil fractions of Oxisols. Muscovite, kaolinite and quartz also present Si in their composition, and as these minerals can occur in different particle size fractions of Oxisols (Kämpf; Marques; Curi, 2012), strong and positive correlations between this element and the particle size fractions of these soils do not happen.

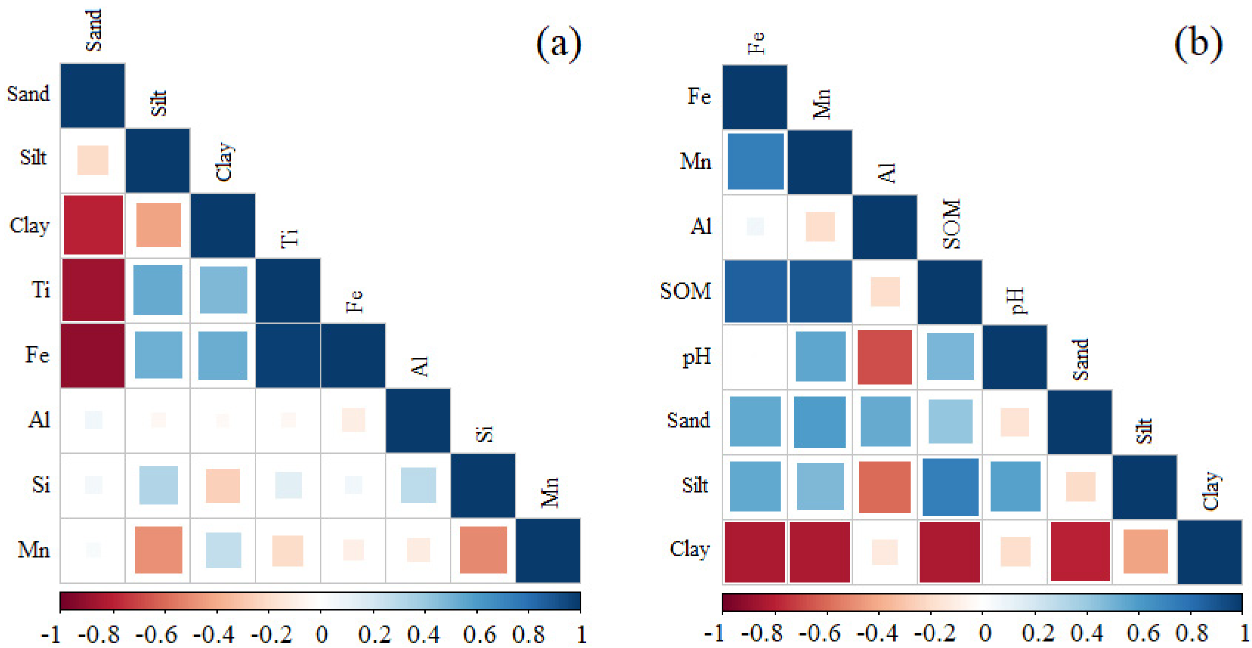

Figure 4: Correlations between soil texture and pXRF data (a) and between soil texture and fertility analyses (b). Data from composite samples of horizons of the Oxisol profiles located at the IFSULDEMINAS, Muzambinho municipality, Minas Gerais state, southeastern Brazil.

Available contents of Fe and Mn had a strong correlation with the SOM (Figure 4b: 0.86 and 0.90, respectively; $p<0.05$), which can be explained by their adsorption onto SOM, due to their opposite superficial electrical charges (Franks et al., 2021; Lana et al., 2014). The available contents of Fe and Mn were negatively correlated to the clay fraction (-0.83 and -0.84; $p<0.05$ respectively), probably because of the low-activity clays in these soils. The relationships between available Fe and Mn contents were strong and positive (0.73; $p<0.05$) because of their similar behavior in Oxisols.

The relations found in Figure 4b between texture and SOM for Oxisols differed from Zinn, Lal and Resck (2005). The mentioned authors detected no significant correlations between clay contents and SOC in soils of the Brazilian Cerrado; yet, here, the clay content had a high negative (-0.83; $p<0.05$) correlation with SOM. This could be related to the different biomes where these Oxisols are situated: soils studied herein belong to the Atlantic Forest biome, which has several different attributes compared to the Cerrado biome (Curi et al., 2017).

The exchangeable Al^{3+} content had a negative correlation (-0.67; $p<0.05$) with soil pH because of the dominance of hydroxide forms of Al as the pH increases, favored by liming application in the superficial horizons of soils in this area (Lopes; Guilherme, 2016).

Geomorphology and pedogenesis

Oxisols are usually associated with stable, flat surfaces, and with hot, humid climate. At the beginning of their formation, when the fresh rock was starting to weather, there should have been no structure developed enough to stop particles from being transported in case the rock was situated in a steep slope. Hence, for the rock to be weathered under hot and humid climate without having its particles eroded away and deposited elsewhere (pedogenesis < erosion), the soils studied here must have formed and deepened for a long period under smooth surfaces (pedogenesis > erosion).

The studied soils, however, are nowadays situated in a very steep slope (Figure 1). Their paradoxical depth and landscape position indicate two aspects: i) they were certainly formed under past landforms; and ii) a lot of weathering and formation happened before these landforms changed significantly. These soils likely developed in a preceding flat surface during intense periods of weathering-leaching. Today, they are progressively exposed as present-day landforms are carved and become steeper (Bigarella, Mousinho, Silva, 2016; Resende et al., 2014). This interpretation is supported by the fact that since a long time ago the Brazilian territory has been submitted to very intense water erosion, and as a consequence some strata from the geologic column, common in another parts of world, are absent in Brazil (Resende et al., 2019).

It is true that soils from temperate regions commonly begin their pedogenetic processes as glaciers recede and form new erosional surfaces (Sanborn, 2016; Tsai et al., 2016) – that is, soils are more closely related to erosion surfaces and their ages. However, soils from the studied area and similar tropical regions in southeastern Brazil have developed continuously since ancient times and are now becoming shallower in some cases, as landforms are carved by recent drainage systems. Many soil classes are thus less related to their respective erosional surfaces, since they were formed previously and are now being dissected.

An important evidence to consolidate this idea is the coinciding altitude of hilltops throughout the region (King, 1956; Resende et al., 2019) (Figure 5). Although altitude differences between regions may exist due to subsidence and other geological processes, many hilltops across large areas have barely the same altitude. This is a clear indication that in the past this region had large portions of flatter relief. The strongly undulated relief observed now indicates an erosion resumption, caused by the lowering of the base level during a somewhat drier climate (Resende et al., 2021). The old, weathered and flat landforms were hence dissected and resulted in a rugged landscape with absence of rock outcrops and many deep, nutrient-poor soils, even in steep slopes.

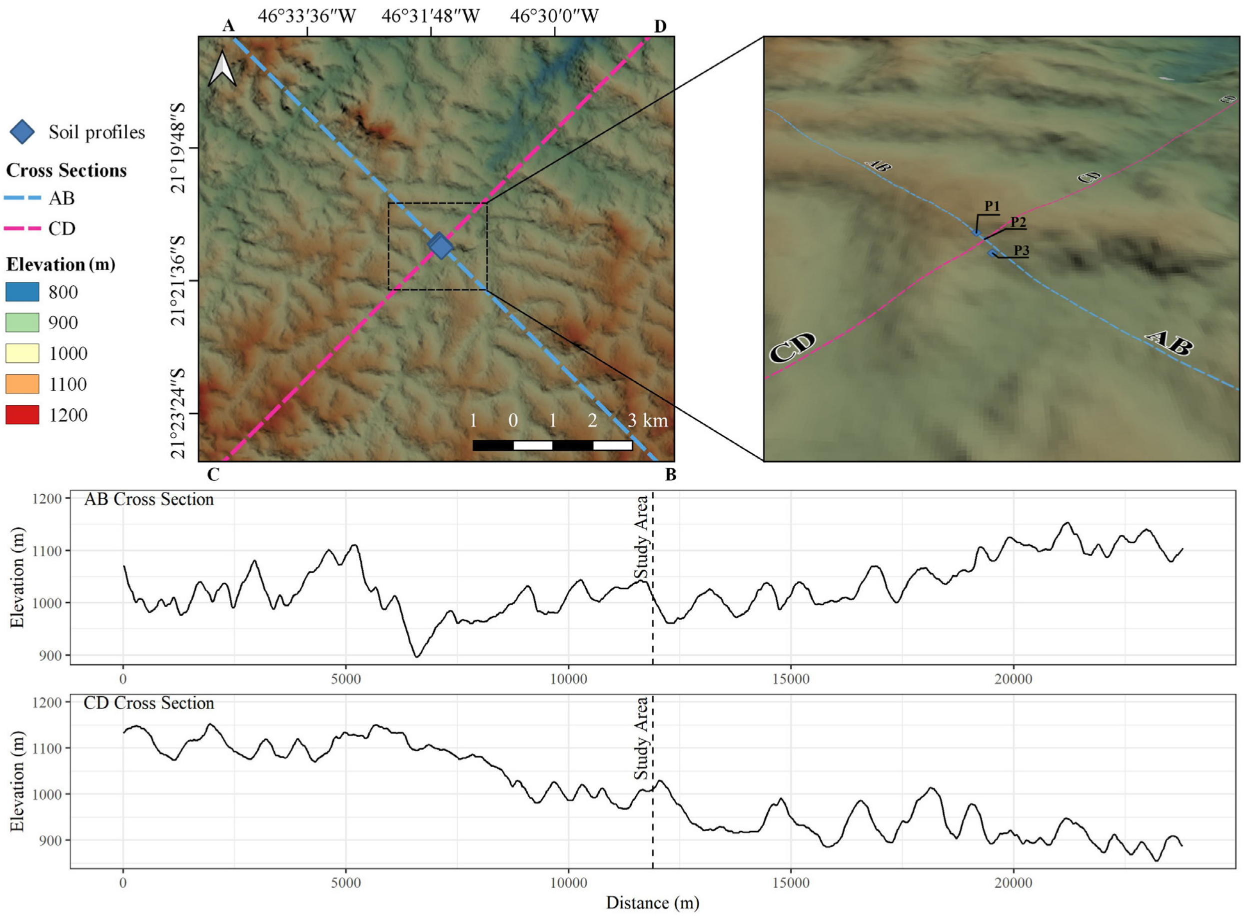

Figure 5: Two cross sections showing the concordance of hilltop altitudes around the study area in the Muzambinho municipality, Minas Gerais state, Brazil. Distance is measured from the points A and C to points B and D. The points were chosen arbitrarily. Dashed lines show the location of the study area within the cross sections. P1: Profile 1; P2: Profile 2; P3: Profile 3.

CONCLUSIONS

Soils were successfully characterized quickly and at low cost with the aid of pXRF. Chemical analysis highlighted traits of the parent material (e.g., Al and Fe contents) and showed that all three studied soils are dystrophic. This is evidence of a deep, nutrient-poor regolith even in lower positions of the hill. The soil weathering indexes calculated from pXRF data showed the advanced stage of aging of these soils even in strongly undulated relief. Weathering degree was higher in Bo horizon than in superficial horizons indicating pre-weathering of these soils. The weathering degree tended to decrease down the slope. The decreasing weathering degree order for the studied soils was: P1 ≥ P2 > P3. The great depth of these soils even in the steepest parts of the slope are evidence that pedogenesis happened mainly prior to current landforms. The idea of a flat paleorelief is supported by the absence of rock outcrops and the concordance of altitude of the surrounding summits, and helps to explain the abnormal soil-landscape relationships observed today in this physiographic region. After their formation, the resumption of erosional processes dissected the landscape, exposing deeper parts of these ancient soils, but not yet reaching the parent rock (gneiss).

AUTHOR CONTRIBUTION

Conceptual idea: Bócoli, F.A.; Santos, W.J.R.; Silva, S.H.G.; Curi, N.; Methodology design: Bócoli, F.A.; Santos, W.J.R.; Data collection: Bócoli, F.A.; Santos, W.J.R.; Data analysis and interpretation: Bócoli, F.A.; Silva, S.H.G.; Teixeira, A.F.S.; Mancini, M.; Curi, N.; and Writing and editing: Bócoli, F.A.; Teixeira, A.F.S.; Mancini, M.; Curi, N.

ACKNOWLEDGMENTS

The authors would like to thank the Programa Institucional de Bolsa de Iniciação Científica (PIBIC) of the Instituto Federal de Educação Ciência e Tecnologia do Sul de Minas Gerais, *Campus* Muzambinho, and the institution facilities and equipments availability to this study realization. Also, we acknowledge CNPq, CAPES and FAPEMIG for financial research support.

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