

Division - Soil Processes and Properties | Commission - Soil Mineralogy

Pedogenic Iron Oxides in Iron-Rich Oxisols Developed from Mafic Rocks

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ABSTRACT: Despite the considerable amount of information on the mineralogical characteristics of pedogenic Fe oxides in Brazilian soils, there are few studies on Fe-rich soils developed from mafic rocks with taxonomic identities at lower categorical levels. This study evaluated the mineralogical characteristics of pedogenic Fe oxides in B horizons (Bw) of Fe-rich Oxisols developed from several mafic rocks in the state of Minas Gerais, Brazil. The Bw horizons were sampled at a 0.8-1.0 m depth in 13 Ferric and Ferrihydric Rhodic Oxisols along with a Mesoferrihydric Typic Oxisol originating from basalt, gabbro, tuffite, amphibolite and itabirite in Minas Gerais. The selected soils have taxonomic identities up to the fourth categorical level of the Brazilian System of Soil Classification. In the laboratory, the following analyses were made: a) powder X ray diffraction (XRD) of the clay fraction before and after selective concentration of Fe oxides by silicate alkaline dissolution (5 mol L⁻¹ NaOH); b) selective chemical dissolution of the clay fraction by citrate-bicarbonate-dithionite (CBD), acid ammonium oxalate (AAO), and sulfuric acid (H₂SO₄ 1.8 mol L⁻¹); c) quantitative estimation of minerals in the clay fraction through allocation of phases from the XRD patterns, magnetic susceptibility of the clay fraction, and quantification of elements after sulfuric acid digestion (H₂SO₄ 1:1) of the air-dried fine earth and treatment of the clay fraction with CBD; and d) estimation of the mean crystal size (MCS), specific surface area (SSA), and isomorphous Al-substitution (IS) of hematite, goethite, and maghemite from the XRD patterns obtained from concentrates of Fe oxides. The results showed that estimation of Fe content of maghemite by selective dissolution with 1.8 mol L⁻¹ H₂SO₄ may not be accurate enough to realistically reflect the maghemite contents in the soil sample. The Al content extracted may also be influenced by other minerals that are sources of this element. Hematite crystals were predominantly placoid in shape in all Rhodic Oxisols and had smaller SSA compared to goethite, which showed both isodimensional and asymmetric habit. Higher crystallinity of maghemite and the IS values generally lower than those of hematite and goethite suggest that in well-drained soils derived from mafic rocks, the IS phenomenon in maghemites seems to result from pedogenetic advancement after its formation from magnetite oxidation.

Keywords: hematite, maghemite, crystallographic characteristics, Al-substitution, selective dissolution.

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INTRODUCTION

Knowledge of the conditions under which Fe oxides (oxides, hydroxides, and oxyhydroxides) are formed in pedogenic and geochemical environments is critical for interpretation of current and past processes in soils (Kämpf and Curi, 2000). These minerals are involved in various soil phenomena, such as in adsorption of anions, cations, and organic compounds, as well as in fixing P and heavy metals. In addition, they are linked to some morphological properties, such as color, structure, and magnetism, inducing the formation of aggregates and cementing of other important soil components, namely nodules, concretions, plinthites, petroplinthites, ortsteins, etc. (Schwertmann and Taylor, 1989).

Goethite (Gt), responsible for yellow color, is the most common antiferromagnetic Fe oxide, followed by hematite (Hm), which causes red coloring in soils (Schwertmann and Taylor, 1989; Kämpf and Curi, 2000; Cornell and Schwertmann, 2003; Fontes and Carvalho Jr., 2005). Maghemite (Mh), ferromagnetic Fe oxide, is common in several soil classes in tropical and subtropical environments (Schwertmann and Taylor, 1989). Although it generally occurs in small amounts in some soil classes, Mh provides high magnetization to soils originating from basic igneous rocks (Fabris et al., 1997a; Costa et al., 1999) and other Fe-rich materials (Costa et al., 2014; Carvalho Filho et al., 2015). In Rhodic Oxisols developed from basic rocks, the Mh content increases considerably and may account for up to 40 % of the mass of the Fe oxide content in the clay fraction (Costa et al., 1999).

Methods of identification, quantification, and characterization of various mineral phases of Fe oxides are particularly important. Some of the main methods used include X ray diffraction (XRD – powder method) and selective chemical dissolution with citrate-bicarbonate-dithionite of sodium (CBD) (Mehra and Jackson, 1960), acid ammonium oxalate (AAO) (McKeague and Day, 1966), and sulfuric acid (Schwertmann and Fechter, 1984).

Despite the high geochemical affinity of Fe with various metals, Al^{3+} is the main isomorphic metal cation substituent in the structure of Fe oxides (IS). The amounts 0.33, 0.15, and 0.33 mol of IS mol⁻¹ are established limits for Gt, Hm, and Mh, respectively (Schwertmann and Kämpf, 1985; Kämpf and Curi, 2000; Cornell and Schwertmann, 2003). Isomorphic substitution is a natural phenomenon and is more a rule than an exception in pedogenic Fe oxides of tropical climate. Generally, higher degrees of isomorphic substitution are associated with weathered soils and with greater Al activity, resulting in considerable changes in the size of the unit cell and crystallinity of the mineral particle (Fontes and Weed, 1991).

Regarding size, Gt usually features an isodimensional crystallization habit and its spherical habit is confirmed by electron microscopy techniques in tropical soils (Schulze and Schwertmann, 1984; Schwertmann and Kämpf, 1985; Melo et al., 2001; Correa et al., 2008) and by similar values for mean crystal size (MCS) in the d_{110} and d_{111} directions obtained by the Scherrer equation (Klug and Alexander, 1954; Fontes and Weed, 1991). However, Melo et al. (2001) also found different MCS values for some samples, and growth was greater in the d_{110} direction. Hematite commonly has the form of circular plates (Schwertmann and Kämpf, 1985; Fontes and Weed, 1991; Melo et al., 2001). Maghemite is usually formed from the transformation of the solid state of other Fe oxides and, for the most part, it adopts the growth habit of its precursor (Cornell and Schwertmann, 2003).

Although several studies have been conducted on Fe oxides in Brazil, few were able to gather a significant volume of soils originating from different parent materials with taxonomic similarities to the Brazilian (SiBCS - Santos et al., 2013) and North American (Soil Survey Staff, 2014) Classification Systems. The Fe-rich Rhodic Oxisols (Soil Survey Staff, 2014) occupy significant areas in the regions of the Central Plateau and the Ferriferous Quadrilateral in Brazil, especially those developed from basalt, tuffite, and itabirite, where, in addition to dystrophic and acric properties, typically feature high

saturation magnetization, although with differences between soils developed from the same parent material (Carmo et al., 1984; Ferreira et al., 1994; Fabris et al., 1997a; Costa et al., 1999; Silva et al., 2005; Silva et al., 2010; Cervi et al., 2014; Costa et al., 2014; Carvalho Filho et al., 2015).

Once the mineralogical variations in pedogenic Fe oxides are determined by the parent material and pedoenvironmental conditions, it is hypothetically assumed that will be possible to observe quantitative and crystallographic differences in these minerals even between groups of taxonomically similar soils. Thus, this study evaluated the mineralogical characteristics of pedogenic Fe oxides in B horizons (Bw) of Fe-rich Oxisols developed from several mafic rocks in the state of Minas Gerais, Brazil.

MATERIALS AND METHODS

Samples were collected from the 0.8-1.0 m depth in different regions of the state of Minas Gerais in the Bw horizons of 13 Rhodic Oxisols originating from various parent materials: ferric (total contents of Fe_2O_3 between 180 and 360 g kg^{-1} - LV₁, LV₂, LV₃, LV₅, LV₆, LV₁₀, LV₁₂, and LV₁₃) and perferic (total contents of Fe_2O_3 higher than 360 g kg^{-1} - LV₄, LV₇, LV₈, LV₉, and LV₁₁). A mesoferric Typic Oxisol was also collected (total contents of Fe_2O_3 between 80 g kg^{-1} and 180 g kg^{-1} - LVA₁) (Figure 1, Table 1). According to the Brazilian System of Soil Classification (SiBCS) (Santos et al., 2013), the taxonomic names ferric, perferic, and mesoferric are based on the Fe content extracted after sulfuric digestion of air-dried fine earth (ADFE), which is obtained from air drying and breaking up soil samples, and then sieving them through a 2-mm mesh (Donagema et al., 2011).

After separation of particle size fractions (Jackson, 1979), minerals of the clay fraction were estimated by the allocation method proposed by Resende et al. (1987) with ALOCA

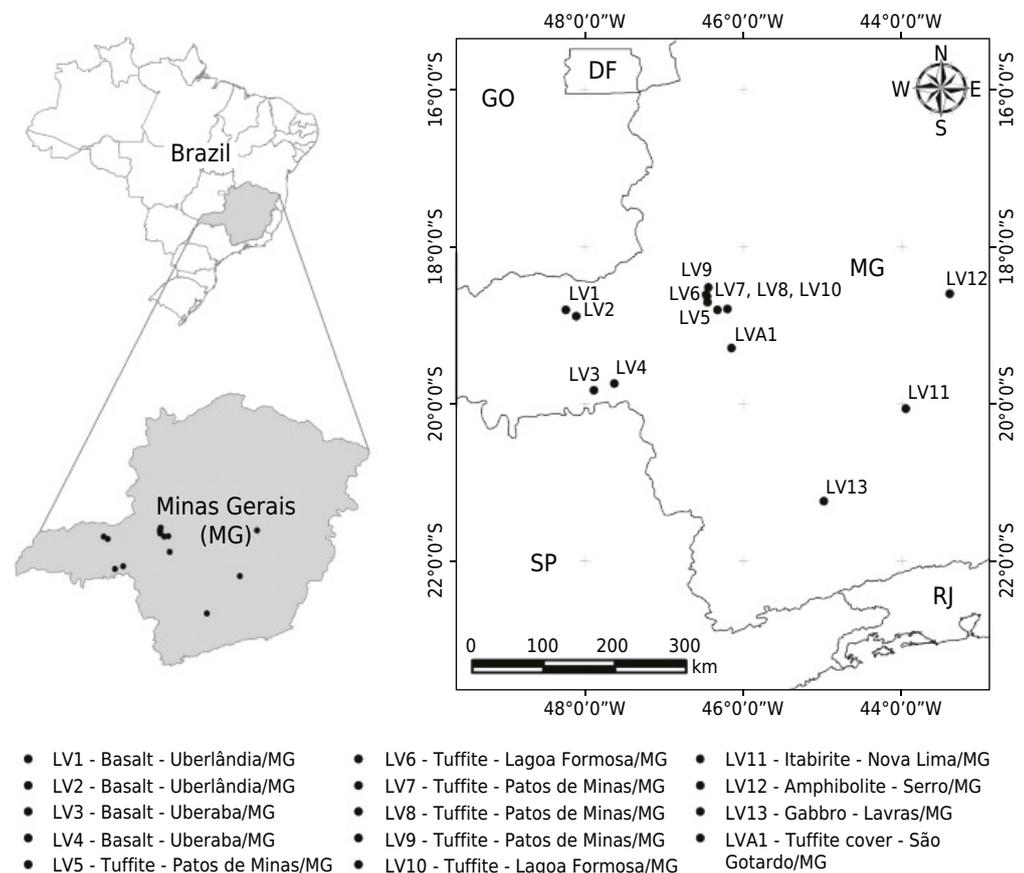


Figure 1. Localization of the soils with their respective parent materials.

Table 1. Soil classification according to the Brazilian System of Soil Classification – SiBCS and U.S. Soil Taxonomy (SSS) and quantitative estimate of the mineralogical assemblage of the clay fraction

SiBCS ⁽¹⁾	SSS ⁽²⁾	K	Gb	Gt	Hm	Mh	An/Rt ⁽³⁾
<i>Latossolo Vermelho Distroférrico típico - LV₁</i>	Rhodic Hapludox	433.1	67.2	23.4	134.4	41.5	22.4
<i>Latossolo Vermelho Acriférrico típico - LV₂</i>	Rhodic Acrudox	175.9	338.5	16.5	93.3	91.0	27.0
<i>Latossolo Vermelho Acriférrico típico - LV₃</i>	Rhodic Acrudox	209.2	273.5	12.2	98.3	91.3	16.8
<i>Latossolo Vermelho Perférrico típico - LV₄</i>	Rhodic Acrudox	139.4	361.3	23.5	117.2	80.3	20.5
<i>Latossolo Vermelho Acriférrico típico - LV₅</i>	Rhodic Acrudox	105.2	437.7	24.5	121.8	57.9	37.3
<i>Latossolo Vermelho Distroférrico típico - LV₆</i>	Rhodic Hapludox	277.2	276.8	52.5	88.3	11.3	54.1
<i>Latossolo Vermelho Perférrico típico - LV₇</i>	Rhodic Hapludox	54.4	228.2	12.0	64.1	161.8	49.7
<i>Latossolo Vermelho Perférrico típico - LV₈</i>	Rhodic Acrudox	127.1	291.9	3.4	110.6	123.6	52.8
<i>Latossolo Vermelho Perférrico típico - LV₉</i>	Rhodic Hapludox	71.4	189.4	n.d.	62.3	208.6	31.3
<i>Latossolo Vermelho Distroférrico típico - LV₁₀</i>	Rhodic Hapludox	154.6	173.0	8.6	130.1	121.8	50.9
<i>Latossolo Vermelho Perférrico típico - LV₁₁</i>	Rhodic Acrudox	21.9	138.2	85.9	226.2	217.1	8.3
<i>Latossolo Vermelho Distroférrico típico - LV₁₂</i>	Rhodic Hapludox	221.1	183.3	60.5	173.7	20.8	17.7
<i>Latossolo Vermelho Acriférrico típico - LV₁₃</i>	Rhodic Acrudox	256.1	259.8	39.3	112.6	41.4	5.6
<i>Latossolo Vermelho-Amarelo Ácrico típico - LVA₁</i>	Typic Acrudox	196.8	435.3	52.9	64.6	1.3	48.3

⁽¹⁾ Santos et al. (2013); ⁽²⁾ Soil Survey Staff (2014); ⁽³⁾ Mineralogical composition estimated by allocation from X ray patterns, sulfuric digestion, CBD, and magnetic susceptibility (Resende et al., 1987). K: kaolinite, Gb: gibbsite, Gt: goethite, Mh: maghemite, Hm: hematite, and An/Rt: anatase and/or rutile; n.d.: not detected.

software (Moura Filho et al., 1995). The chemical elements of minerals in the clay fraction [extracted by sulfuric digestion with ADFE (1:1 ratio with H₂SO₄) (Donagema et al., 2011) and by five successive extractions with dithionite-citrate-bicarbonate of sodium (CBD) at 80 °C (Mehra and Jackson, 1960)] were allocated in the minerals identified by X ray diffraction (XRD) in the same clay fraction without treatment (natural clay). Diffractograms of X rays were obtained in the X'Pert Pro Panalytical device with CoK α radiation, operating at 40 kV and 30 mA. The scan range was 4 to 50 °2 θ , with an interval of 0.01 °2 θ s⁻¹.

Magnetic susceptibility per mass unit was quantified by measuring at low frequency (0.47 kHz) through a Bartington MS2 system (Bartington Instruments LTD, Oxford, England), coupled to an MS2B sensor (Dearing, 1999). Determining magnetic susceptibility in the clay fraction allowed the Mh rate in soil to be estimated (Resende et al., 1987).

In addition to the sequential extractions with CBD for complete removal of pedogenic Fe oxides, including the crystalline (basically Gt, Hm, and Mh) and low crystalline (ferrihydrite - Fr) (Fe_d) forms (Mehra and Jackson, 1960), natural clay samples were also subjected to a single extraction with 0.2 mol L⁻¹ acid ammonium oxalate (AAO) at pH 3 for removal of only Fe from the low crystallinity phases (Fe_o) (McKeague and Day, 1966). For selective Fe dissolution of Mh, the clay fraction was subjected to only one extraction

with $1.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at $80 \text{ }^\circ\text{C}$ for 2 h ($\text{Fe}_{\text{H}_2\text{SO}_4}$) (Schwertmann and Fechter, 1984, modified by Costa et al., 1999). The contents of Fe and Al solubilized by the CBD, AAO, and H_2SO_4 extractants were determined by atomic absorption spectroscopy.

Concentrates of Fe oxides were obtained by selective dissolution of silicate minerals in the clay fraction, using $5\text{-mol L}^{-1} \text{ NaOH}$ solution under heating (Norrish and Taylor, 1961; Kämpf and Schwertmann, 1982). The mineral components of concentrated samples were identified by XRD with scanning from 4 to $80 \text{ }^\circ 2\theta$. The samples were ground in an agate mortar along with 10% silicon, used as an internal standard for correction of distortions (position and width of half-height of peaks), and mounted on slides excavated without guidance (powder).

The Hm/(Hm+Gt) ratio was estimated based on reflex areas of d_{012} of Hm and d_{110} of Gt in Fe oxide concentrates. The formula used for calculation was suggested by Resende et al. (1987): $[\text{Hm}/(\text{Hm} + \text{Gt})] = 4 \times A_{\text{Hm}012}/(4 \times A_{\text{Hm}012} + A_{\text{Gt}110})$, in which A is an area of the respective reflexes.

The mean crystal size (MCS) was calculated from the width of the half-height of reflexes d_{110} and d_{111} of Gt, d_{104} , d_{110} , and d_{012} of Hm, and d_{220} and d_{400} of Mh, using the Scherrer equation (Klug and Alexander, 1954). The instrumental error correction was made using the adjustment equation established by Melo et al. (2001) from the data presented by Klug and Alexander (1954) for low and moderate Bragg angles ($^\circ 2\theta$). Next, values of the specific surface area (SSA) were determined for Gt and Hm. For Gt, the isodimensional shape (sphere) was adopted (Schulze and Schwertmann, 1984; Schwertmann and Kämpf, 1985; Fontes and Weed, 1991; Melo et al., 2001): $\text{SSA}_{\text{Gt}} = (1049/\text{MCS}_{100}) - 5 \text{ (m}^2 \text{ g}^{-1})$, in which $\text{MCS}_{100} = d_{110} \times 0.42 \text{ nm}$ (Schulze and Schwertmann, 1984; Schwertmann and Kämpf, 1985). For Hm, the shape of round plates was adopted (Schwertmann and Kämpf, 1985; Fontes and Weed, 1991; Melo et al., 2001), and the geometric shape of a cylinder was used: $\text{SSA}_{\text{Hm}} = 2 \times (r + h) \times 10^3/r \times h \times d \text{ (m}^2 \text{ g}^{-1})$, in which $r = \text{MCS}_{110} \times 0.71/2$, $h = \text{MCS}_{012} \times 0.59$, and $d = 5.26 \text{ g cm}^{-3}$ (Schwertmann and Kämpf, 1985).

According to the Vegard Law, the occurrence and magnitude of isomorphic substitution of Fe by Al (IS) may be quantified from the regression between the volume of the mineral unit cell and the degree of IS $[\text{Al}/(\text{Fe}+\text{Al}), \text{mol mol}^{-1}]$. IS in the structure of Gt, Hm, and Mh was estimated by the position of the reflexes of these minerals obtained by XRD in the concentrates of Fe oxides. The position of the silicon peaks in each sample was used for instrumental corrections. In Gt, IS was calculated using the equation $\text{Al (mol mol}^{-1}) = 17.30 - 5.72 \times c_0$, in which the c_0 size of the unit cell in Gt is obtained from d_{110} and d_{111} reflexes by $c_0 = (1/d_{111}^2 - 1/d_{110}^2)^{0.5}$ (Schulze, 1984). For Hm, the equation $\text{Al (mol mol}^{-1}) = 31.09 - 6.17 \times a_0$ was used, in which the a_0 size of the unit cell in Hm is obtained by d_{110} reflexes for $a_0 = 2 \times d_{110}$ (Schwertmann et al., 1979). In Mh, IS was estimated by the equation $\text{Al (mol mol}^{-1}) = [0.8343 - a_0] / 2.22 \times 10^{-4}$, in which a_0 corresponds to the size of the unit cell in Mh perpendicular to plane d_{220} (Schwertmann and Fechter, 1984).

The Pearson correlations between the variables analyzed were determined using the statistical software Statistic v.9 (Carvalho Filho et al., 2015).

RESULTS AND DISCUSSION

Mineralogical composition of the clay fraction

The mineralogical constituents identified in the clay fraction were kaolinite, goethite, hematite, maghemite, gibbsite, anatase, and rutile at different rates, even in taxonomically related soils originating from the same parent material (Table 1). In quantitative terms, these results disagree with the general idea of mineralogical homogeneity for Oxisols (Resende et al., 1987).

The oxide dominance in the clay fraction, essentially gibbsite, hematite, maghemite, and anatase, is a consequence of the significant loss of exchangeable cations and silica (ferralitization), promoting accumulation of residual minerals in soils, as well as the desilicated nature of the parent materials (Carmo et al., 1984; Melo et al., 2001; Costa et al., 2014; Carvalho Filho et al., 2015). Only LV₁ showed a significant amount of kaolinite, possibly due to the influence of detrital sediments on the soil surface in South America (King, 1956).

Hematite (Hm) is the main antiferromagnetic Fe oxide in soils and its maximum content was observed in LV₁₁ (perferric) (226.2 g kg⁻¹), formed from itabirite (Table 1). However, a considerable amount of goethite (Gt) was also observed in LV₁₁, which was not expressed in color because of the high pigmentation power of Hm (Resende, 1976; Fontes and Carvalho Jr., 2005). The same behavior was observed in LV₁₂. Curi and Franzmeier (1987) reported the presence of significant quantities of Gt, higher than Hm, in a Rhodic Oxisol formed from itabirite. The authors highlight that the lithogenetic heritage of Gt, concentrated in its pigmentation effect on the coarse fraction (sand and silt), explains the redder colors in soils formed from basalt, with Hm contents greater than Gt contents.

The occurrence of Hm and Gt oxides in soils is generally assigned to neoformation from the weathering of primary minerals containing Fe in their structure, or inherited directly from the parent material, as reported for Hm (Barbosa and Lagoeiro, 2010; Costa et al., 2014; Ávila et al., 2015) and Gt (Curi and Franzmeier, 1987) of ferriferous formations in the Ferriferous Quadrilateral in Minas Gerais. However, the predominance of Hm or Gt is controlled by the environmental conditions of soil formation (Curi and Franzmeier, 1984; Schwertmann and Taylor, 1989; Kämpf and Curi, 2000). The higher Fe content, common in soils from mafic rocks, associated with a lower degree of moisture, favored Hm formation and the predominance of this mineral over Gt in all soils studied. In contrast, LV₆ (3.5 YR hues) and LVA₁ (5 YR hue) had nearly equal Hm and Gt contents, indicating wetter pedoenvironmental conditions.

Maghemite (ferromagnetic Fe oxide - Mh) occurred in all soils, even if virtually inexpressive in LVA₁ and LV₆ (Table 1). In Brazil, for soils developed from mafic rocks, Mh formation is more associated with magnetite oxidation inherited from the parent material (Curi and Franzmeier, 1987; Fontes and Weed, 1991) as well as transformation from other magnetic phases, such as magnesiumferrite commonly found in tuffite and in the sand fraction of soils originating from it (Fabris et al., 1997b; Silva et al., 2005). However, under conditions of redox oscillations that occur during the wetting and drying cycles, fine magnetite grains may also be formed and subsequently oxidized, giving rise to Mh (Maxbauer et al., 2016). Although less common, another formation of Mh under field conditions is from transformation of other pedogenic Fe oxides (Hm and Gt) when under high temperatures in the presence of organic C (Curi and Franzmeier, 1987; Fontes and Weed, 1991; Costa et al., 1999; Fontes et al., 2000). The low expression of Mh in LV₆ and LVA₁ might be attributable to lithological variations and/or preferential dissolution of Mh rather than Hm in wetter pedoenvironments (Curi and Franzmeier, 1984).

The presence of Mh, in some cases at higher rates than Hm or Gt (LV₇, LV₈, and LV₉), highlights the need to quantitatively use the Mh contents or the magnetic properties of soils as criteria for taxonomic separation, especially for the Fe-rich Rhodic Oxisols (Carvalho Filho et al., 2015). In these cases, there is inconsistency in the exclusive use of color, dictated by the ratio Hm/(Hm + Gt) as criterion of the second-level category (suborder) in SiBCS (Santos et al., 2013). This consideration also applies to international classification systems, such as Soil Taxonomy (Soil Survey Staff, 2014) and the World Reference Base (IUSS, 2015), which do not have criteria for separating soil according to magnetic properties.

Anatase and/or rutile, Ti oxides in soils developed from common igneous and metamorphic rocks (Taylor et al., 1983), also occurred in the clay fraction of all the soils studied

(Table 1). The genesis of these minerals may be related to weathering of minerals, such as ilmenite, or linked to the release of Ti during the weathering of silicates, such as pyroxene, amphibole, and biotite (Taylor et al., 1983). Anatase may also originate from Ti-magnetite (Taylor et al., 1983), fairly common in tuffite soils (Fabris et al., 1994). Soils formed from tuffite (LV₅, LV₆, LV₇, LV₈, LV₉, LV₁₀, and LVA₁) had higher contents of anatase/rutile, exceeding the maximum limit of 30 g kg⁻¹ generally found in the clay fraction of soils (Jackson, 1964). Rutile from XRD of Fe oxide concentrates also occurred in these soils (Figure 2). This shows the high influence of the parent material on Ti oxide content in the soil clay fraction.

Selective dissolution of Fe oxides

In general, all soils exhibited high contents of Fe_d, reaching 480.5 g kg⁻¹ of clay in soil LV₁₁ (perferric). High Fe_d contents were also found by other authors for soils formed from itabirite (Table 2) (Curi and Franzmeier, 1987; Costa et al., 2014; Carvalho Filho et al., 2015). The lowest contents of Fe_d and Fe_{H2SO4} were observed in LV₆ and LVA₁, suggesting both lower Fe content in the parent material, due to tuffite heterogeneity

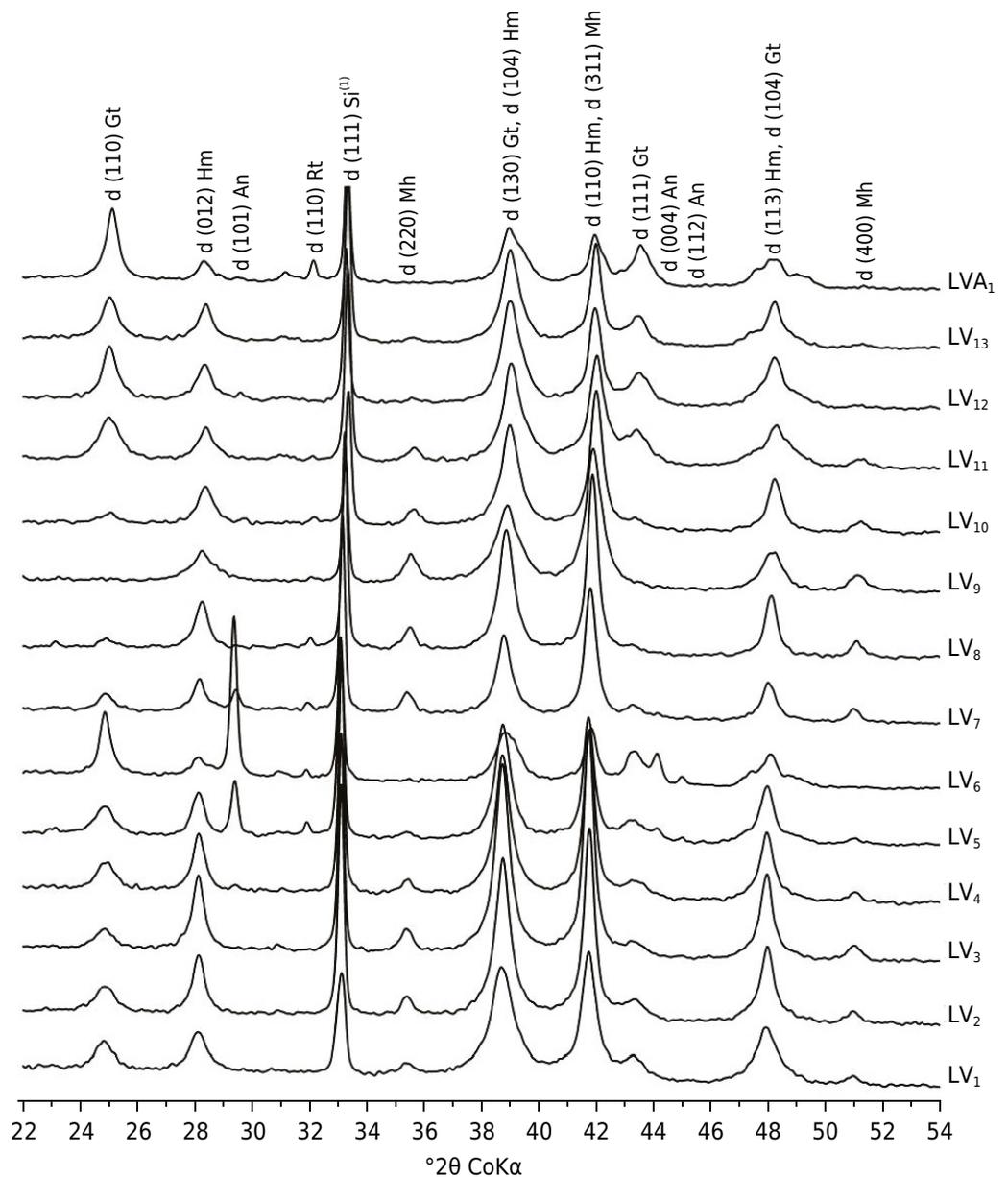


Figure 2. X ray patterns from the clay fraction after treatment for Fe oxide concentration. ⁽¹⁾ Internal standard used.

(Guimarães, 1955), and deferrification processes occurring in wetter pedoenvironments (Curi and Franzmeier, 1984; Schwertmann and Taylor, 1989; Kämpf and Curi, 2000).

At least five successive extractions with CBD were required for total removal of the Fe contained in pedogenic Fe oxides (Figure 3). The slope of curves of cumulative Fe_d contents were lower in soils with greater participation of Gt (LVA_1 and LV_6). Conversely, Inda Junior and Kämpf (2003) highlighted that two successive extractions with CBD, heated at 80 °C, are enough to extract almost all (>98 %) pedogenic Fe oxides, regardless

Table 2. Silicon, Al, Fe, and Ti contents determined by sulfuric digestion of ADFE (Si_s , Al_s , Fe_s , and Ti_s) and Fe and Al obtained in the clay fraction by sequential extractions with citrate-bicarbonate-dithionite (CBD) (Fe_d and Al_d), only one extraction with acid oxalate ammonium (AAO) (Fe_o and Al_o) and 1.8 mol L⁻¹ H₂SO₄ ($Fe_{H_2SO_4}$ and $Al_{H_2SO_4}$) all presented as oxides

Soil	Sulfuric digestion				CBD		AAO		1.8 mol L ⁻¹ H ₂ SO ₄		Fe _o	Fe _d	Fe _{H₂SO₄}	Fe _{H₂SO₄}	IS _d ⁽¹⁾	IS _{H₂SO₄} ⁽²⁾
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	Fe _d	Fe _s	Fe _d	Fe _s	mol mol ⁻¹	
	g kg ⁻¹															
LV ₁	201.4	222.3	310.7	69.7	189.5	25.5	10.2	8.5	85.5	119.1	0.05	0.61	0.45	0.28	0.174	0.686
LV ₂	81.8	303.5	345.1	71.8	186.2	20.8	12.0	10.4	77.3	173.0	0.06	0.54	0.42	0.22	0.149	0.778
LV ₃	97.3	272.0	330.0	71.7	189.9	19.7	10.2	10.0	80.0	199.9	0.05	0.58	0.42	0.24	0.139	0.797
LV ₄	64.8	303.1	370.8	71.5	206.6	23.0	11.2	10.2	75.1	176.0	0.05	0.56	0.36	0.20	0.148	0.786
LV ₅	48.9	340.3	293.0	60.0	189.1	23.8	8.2	10.2	73.7	196.7	0.04	0.65	0.39	0.25	0.164	0.807
LV ₆	128.9	307.3	235.4	69.6	129.7	39.4	10.1	13.6	67.0	146.3	0.08	0.55	0.52	0.28	0.322	0.774
LV ₇	25.3	178.5	459.2	107.3	228.8	26.0	19.4	10.2	84.6	142.4	0.08	0.50	0.37	0.18	0.151	0.725
LV ₈	59.1	250.6	372.0	84.3	227.8	23.9	17.4	9.6	78.3	129.7	0.08	0.61	0.34	0.21	0.141	0.722
LV ₉	33.2	158.2	438.4	107.6	264.8	40.4	35.4	15.3	93.7	142.1	0.13	0.60	0.35	0.21	0.193	0.704
LV ₁₀	71.9	187.7	315.6	79.3	246.1	36.3	22.4	12.2	78.8	117.7	0.09	0.78	0.32	0.25	0.187	0.700
LV ₁₁	10.2	138.3	579.4	21.1	480.5	126.2	25.6	11.1	94.9	91.5	0.05	0.83	0.20	0.16	0.291	0.602
LV ₁₂	102.8	235.5	286.2	28.3	220.1	38.9	8.7	12.9	71.1	106.7	0.04	0.77	0.32	0.25	0.216	0.702
LV ₁₃	119.1	287.5	257.4	16.3	172.7	29.4	5.3	8.0	73.4	161.4	0.03	0.67	0.42	0.29	0.210	0.775
LVA ₁	91.5	373.1	161.4	48.3	102.4	30.9	3.1	9.8	26.4	166.4	0.03	0.63	0.26	0.16	0.320	0.908

⁽¹⁾ Isomorphic substitution of Fe by Al calculated from the molar ratio of the elements extracted by CBD, in which $IS_d = [Al_d / (Al_d + 0.483Fe_d)]$ (Cornell and Schwertmann, 2003); ⁽²⁾ Isomorphic substitution of Fe by Al calculated from the molar ratio of the elements extracted by 1.8 mol L⁻¹ H₂SO₄ in which $IS_{H_2SO_4} = [Al_{H_2SO_4} / (Al_{H_2SO_4} + 0.483Fe_{H_2SO_4})]$ (Cornell and Schwertmann, 2003).

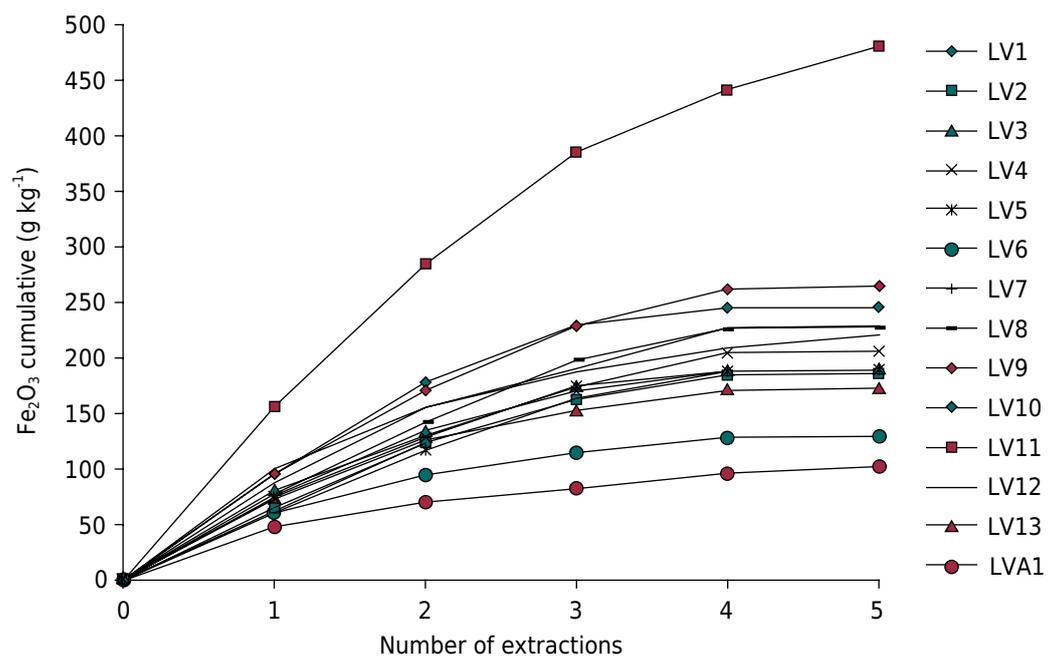


Figure 3. Cumulative iron content throughout the five sequential extractions with citrate-bicarbonate-dithionite in the clay fraction.

of the oxide content in the samples. This was not confirmed by Gualberto et al. (1987) and Corrêa et al. (2015), who reported the need for more than four extractions, due to the significant influence of crystallinity and isomorphic substitution of Fe by Al on the stability of Fe oxides in soils (Inda Junior and Kämpf, 2005; Correa et al., 2008; Corrêa et al., 2015; Carvalho Filho et al., 2015). Fontes (1988) observed that the slopes of the curves of cumulative Fe were higher as Hm and Gt showed lower isomorphic substitution of Fe by Al. The author concluded that only two extractions would not be enough to extract most aluminous Gt.

The Fe contents obtained from sulfuric digestion (Fe_s) ($r = 0.92$, $p < 0.01$, $n = 14$), Fe_d ($r = 0.80$, $p < 0.01$, $n = 14$), and $Fe_{H_2SO_4}$ ($r = 0.72$, $p < 0.01$, $n = 14$) correlated with the Mh contents, which does not occur when these materials correlate with the ratios $Fe_{H_2SO_4}/Fe_s$ and $Fe_{H_2SO_4}/Fe_d$. These observations confirm the association of Mh with the Fe content in the parent material (Costa et al., 1999; Silva et al., 2010; Carvalho Filho et al., 2015) and show the low efficiency of the method of selective dissolution with $1.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ to quantify Fe from Mh. Costa et al. (1999) made changes to the original method of Schwertmann and Fechter (1984) by suggesting 2 h of extraction in an acidic solution rather than 7.5 h for different soil classes and parent materials. Inda et al. (2013) used 45 min for Argissols. This shows the high empiricism of the method and emphasizes the need to conduct further studies to establish appropriate protocols for Fe-rich Oxisols.

The Fe contents extracted by ammonium oxalate (Fe_o), usually lower than 20 g kg^{-1} (Table 2), resulted in a low Fe_o/Fe_d ratio, indicating the dominance of crystalline forms of Fe oxides, characteristic of more developed Oxisols. With the exception of tuffite-originated soils (LV_6 , LV_7 , LV_8 , LV_9 , and LV_{10}), values < 0.06 for the Fe_o/Fe_d ratio were observed. Kämpf et al. (1988) established the lower limit of 0.03 for the order of Oxisols in different regions of Brazil. The highest ratio values were established for most tuffite soils, especially in LV_9 (0.13), which reflects the lower degree of evolution of these soils compared to the others with shorter oxide crystallization time. The main implications of low crystallinity minerals in soils are related to relevant participation in their chemical properties, especially with regard to sorption reactions (Fontes and Weed, 1996).

The Fe_d/Fe_s ratio, which indicates the participation of Fe forms linked to pedogenic Fe oxides in relation to total Fe sulfuric digestion (Fe_s) (Rolim Neto et al., 2009), was low, except for LV_{11} . In Oxisols, the ratio should be between 0.8 and 1.0 (Kämpf et al., 1988). Resende et al. (2011) attribute this result to the high Fe_s values arising from the breakdown of other forms of more crystalline Fe in the coarse fractions (sand and silt from ADFE). However, in Oxisols, the lowest Fe_d/Fe_s ratios were always associated with yellowish soils, due to preferential dissolution of Mh and Hm and greater resistance of Gt, which was largely replaced by Al for reduction by CBD (Torrent et al., 1987; Fontes, 1988).

The values for isomorphic substitution of Fe by Al (IS_d), calculated by the ratio of molar concentration $Al_d/(Al_d + Fe_d)$, ranged from 0.139 to 0.322 mol mol^{-1} (Table 2), consistent with results commonly found by other authors in studies on highly weathered soils from tropical and subtropical regions (Curi and Franzmeier, 1987; Fontes and Weed, 1991; Kämpf and Curi, 2000; Inda Junior and Kämpf, 2005; Correa et al., 2008; Corrêa et al., 2015) and also within the maximum limits established for the structures of Gt and Mh ($0.33 \text{ mol mol}^{-1}$) and Hm ($0.15 \text{ mol mol}^{-1}$) (Cornell and Schwertmann, 2003). The indirect relationship between slope of the curves of the cumulative Fe_d contents (Figure 3) and the IS_d values confirm the stabilizing effect of Al on Gt structure (Torrent et al., 1987; Fontes, 1988; Inda Junior and Kämpf, 2005; Carvalho Filho et al., 2015) in LV_6 and LVA_1 .

The positive correlation between contents of Al_d and Fe_d (0.85 , $p < 0.01$, $n = 14$), as well as the negative correlation between contents of Al_d and Al obtained by sulfuric digestion

(Al_s) ($r = -0.53$, $p < 0.05$, $n = 14$), indicate that the Al contents obtained by successive extractions with CBD are predominantly from the structure of Fe oxides, with negligible performance of other possible sources of this element, such as gibbsite and/or kaolinite (Inda Junior and Kämpf, 2003). This hypothesis is consistent with the absence of correlation between IS_d and Al_s .

Conversely, higher contents of $Al_{H_2SO_4}$, not correlated with those of $Fe_{H_2SO_4}$, suggest the contribution of Al sources, besides Mh, extracted after selective dissolution with $1.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. In addition, the values for isomorphous substitution of Fe by Al ($IS_{H_2SO_4}$) calculated by the ratio of molar concentration $Al_{H_2SO_4}/(Al_{H_2SO_4} + Fe_{H_2SO_4})$ were higher than those for the Mh structure (Cornell and Schwertmann, 2003) and correlated with the contents of Al_s ($r = 0.90$, $p < 0.01$, $n = 14$), reinforcing the hypothesis of contribution of other Al sources (Costa et al., 1999).

Crystallographic characteristics of Fe oxides

The values of the Hm/(Hm+Gt) ratio between 0.55 and 1.00 indicate the higher rate of Hm in relation to Gt in all soils, explaining hues redder than 3.5 YR, with the exception of LVA₁ (5 YR hue) (Table 3). The main factors that favor Hm formation in the soil, and therefore compete to increase this ratio, are greater Fe contents in the parent material, high temperatures, lower humidity, lower organic matter content, and higher pH values (Schwertmann and Taylor, 1989). In this study, excluding the LV₁₁ sample, the value of the linear correlation coefficient between the Hm/(Hm+Gt) ratio and the Fe_d and Fe_s contents increased from 0.24 (ns, $n = 14$) to 0.88 ($p < 0.01$, $n = 13$) and from 0.44 (ns, $n = 14$) to 0.80 ($p < 0.01$, $n = 13$), respectively. This fact, in addition to indicating that the Fe content in the parent material was essential in the formation of Fe oxides (Melo et al., 2001; Carvalho Filho et al., 2015), suggests that LV₁₁ ($Fe_s = 570.4 \text{ g kg}^{-1}$), originating from itabirite, shows significant amounts of Gt obtained from the parent material (Curi and Franzmeier, 1987).

The d-spacing (d) for Fe oxides (Hm, Gt, and Mh) in various directions (*hkl*) was corrected using Si as an internal standard (Table 3). The values were homogeneous overall; however, formed on the same parent material. The d_{110} and d_{111} reflexes of Gt were measured in all soils except for LV₉ (Figure 2).

The values of MCS_{Gt} , perpendicular to planes d_{110} and d_{111} , showed relative agreement with the values observed by other authors for Brazilian soils (Schwertmann and Kämpf, 1985; Curi and Franzmeier, 1987; Fontes and Weed, 1991; Melo et al., 2001; Carvalho Filho et al., 2015). The results for the MCS_{Gt110}/MCS_{Gt111} ratio ranged from 0.95 to 2.63 (Table 3) and showed differences among the crystal morphologies in this mineral. Although some samples showed values of this ratio close to one, in others, the values are far higher (over 1.4), contrary to the common trend of equidimensionality of Gt along the three crystallographic axes (xyz) (Schwertmann, 1988). According to Schwertmann (1988), acicular crystals, in which MCS_{Gt110} is greater than MCS_{Gt111} , are observed in Gt, displaying preferred growth along the z direction. However, the occurrence of both isodimensional and acicular Gt is common in Brazilian soils (Schwertmann and Kämpf, 1985; Fontes and Weed, 1991; Melo et al., 2001; Cornell and Schwertmann, 2003).

There is a great range of estimated values for SSA_{Gt} (32.2 to $157.2 \text{ m}^2 \text{ g}^{-1}$), as well as for IS_{Gt} (0.150 to $0.296 \text{ mol mol}^{-1}$) (Table 3), both within the range of common values in pedogenetic environments (Carvalho Filho et al., 2015). The influence of IS on crystal size reduction of Gt (Schulze and Schwertmann, 1984; Schwertmann and Kämpf, 1985) was confirmed by the significant correlation between the values of IS_{Gt} and SSA_{Gt} ($r = 0.81$, $p < 0.01$, $n = 13$) (Figure 4a). The same result was observed correlating IS_{Gt} with MCS_{Gt110} ($r = -0.69$, $p < 0.01$, $n = 13$) (Schwertmann and Kämpf, 1985; Fontes and Weed, 1991; Melo et al., 2001).

Table 3. d-spacing (d) corrected, mean crystal size (MCS), specific surface area (SSA), isomorphous substitution of Fe by Al (IS) in goethite (Gt), hematite (Hm), and maghemite (Mh), and Hm/(Hm + Gt) ratio for the clay fraction

Soil	d-spacing							MCS							MCS ratios ⁽²⁾			Hm/ (Hm+Gt)	SSA		IS		
	Gt ₁₁₀	Gt ₁₁₁	Hm ₀₁₂	Hm ₁₀₄	Hm ₁₁₀	Mh ₂₂₀	Mh ₄₀₀	Gt ₁₁₀	Gt ₁₁₁	Hm ₀₁₂	Hm ₁₀₄	Hm ₁₁₀	Mh ₂₂₀	Mh ₄₀₀	A	B	C		Gt	Hm	Gt	Hm	Mh
nm																	m ² g ⁻¹		mol mol ⁻¹				
LV ₁	0.416	0.243	0.369	0.271	0.251	0.295	0.208	26.57	14.86	24.33	13.93	30.83	38.91	47.93	1.79	1.55	0.81	0.85	89.0	43.9	0.175	0.057	0.033
LV ₂	0.416	0.242	0.372	0.269	0.251	0.294	0.208	17.03	13.82	33.54	20.04	39.74	45.41	36.04	1.23	1.45	1.26	0.85	141.7	36.4	0.296	0.154	0.125
LV ₃	0.414	0.242	0.366	0.269	0.251	0.294	0.208	15.22	16.00	33.55	20.04	39.73	27.46	24.29	0.95	1.45	1.13	0.89	159.1	36.5	0.270	0.130	0.194
LV ₄	0.413	0.242	0.367	0.270	0.251	0.294	0.208	15.23	13.23	29.89	20.03	34.82	54.49	47.94	1.15	1.42	1.14	0.83	159.0	42.3	0.253	0.106	0.163
LV ₅	0.413	0.242	0.367	0.269	0.251	0.294	0.207	19.36	11.29	24.58	20.04	34.82	30.44	32.14	1.71	1.73	0.95	0.83	124.0	34.8	0.171	0.125	0.175
LV ₆	0.414	0.243	0.367	0.269	0.250	n.d.	n.d.	38.02	14.47	22.60	11.55	23.47	n.d.	n.d.	2.63	1.27	n.d.	0.63	60.7	70.4	0.176	0.188	n.d.
LV ₇	0.415	0.242	0.367	0.270	0.251	0.294	0.208	20.78	17.89	38.27	20.04	34.83	23.01	36.05	1.16	1.11	0.64	0.84	115.2	54.1	0.207	0.147	0.129
LV ₈	0.416	0.243	0.367	0.269	0.251	0.294	0.208	66.47	46.55	22.60	18.75	46.30	30.44	24.29	1.43	2.50	1.25	0.97	32.6	18.1	0.150	0.126	0.174
LV ₉	n.d.	n.d.	0.368	0.269	0.251	0.294	0.208	n.d.	n.d.	17.15	11.55	18.94	21.31	18.43	n.d.	1.35	1.16	1.00	n.d.	82.0	n.d.	0.148	0.151
LV ₁₀	0.416	0.243	0.367	0.270	0.251	0.294	0.208	26.78	23.58	19.49	15.76	31.04	27.46	26.42	1.14	1.94	1.04	0.94	88.3	34.7	0.191	0.145	0.108
LV ₁₁	0.417	0.242	0.367	0.270	0.251	0.294	0.207	17.03	12.68	20.92	17.63	18.94	21.31	19.61	1.34	1.10	1.09	0.72	141.7	100.1	0.260	0.167	0.192
LV ₁₂	0.414	0.242	0.366	0.269	0.251	0.294	0.207	20.78	13.22	19.49	13.03	23.47	34.17	59.26	1.57	1.47	0.58	0.74	115.2	60.7	0.224	0.171	0.127
LV ₁₃	0.416	0.242	0.367	0.269	0.251	0.295	0.208	20.78	19.03	26.97	18.76	31.04	18.57	19.60	1.09	1.40	0.95	0.74	115.2	48.0	0.227	0.146	0.085
LVA ₁	0.414	0.242	0.368	0.269	0.251	n.d.	n.d.	33.32	19.04	29.89	12.00	21.72	n.d.	n.d.	1.75	0.89	n.d.	0.55	70.0	108.7	0.207	0.095	n.d.

⁽¹⁾ d-spacing corrected using silicon as an internal standard. Hm/(Hm + Gt), MCS, SSA and IS ratios were calculated from the X ray patterns of the concentrated Fe oxides; n.d. not detected; ⁽²⁾ Ratios calculated from the MCS values: A = MCS_{Gt110}/MCS_{Gt111}, B = MCS_a/MCS_c = (MCS_{Hm110} × 0.72)/ (MCS_{Hm012} × 0.59), C = MCS_{Mh220}/MCS_{Mh400}.

The great variation in SSA_{Gt} values in tuffite soils highlights the occurrence of Gt with different degrees of crystallinity between soils originating from the same parent material. In this case, besides the possibility of variation in pedoenvironmental conditions favorable to the occurrence of IS, tuffites are basic unhardened heterogeneous rocks, with various proportions of pyroclastic debris and, consequently, different elementary levels (Guimarães, 1955), which may also cause variations in mineral crystallinity. Another aspect is the clear difference of the soil under the influence of detrital materials in the South American plain (LV₁), where SSA_{Gt} and IS_{Gt} values were well below those observed in the other basalt soils.

There was no correlation between IS_{Gt} and the contents of Al_s, disagreeing with the general trend observed in Brazilian soils (Costa et al., 2014). The direct relationship between IS_{Gt} and Al activity in the soil indicates a pedogenetic environment with strong desilication, where Al would be more susceptible to be incorporated into the Gt structure (Schwertmann and Kämpf, 1985). However, generalizations should be avoided because the intensity of this phenomenon cannot be based solely on Al availability in the system. Gibbsite formation is competitive to IS in Gt, that is, environments with high Al contents may prioritize gibbsite formation and reduce IS in Fe oxides.

In general, higher values of MCS_{Hm} were observed compared to those obtained for Gt (Table 3), mainly in the d₁₁₀ direction. This was also verified by other authors (Schwertmann and Kämpf 1985; Kämpf et al., 1988; Fontes and Weed, 1991; Melo et al., 2001, Carvalho Filho et al., 2015), indicating greater development of crystals in the x-y direction compared to the z direction. According to Fontes and Weed (1991) and Melo et al. (2001), this pattern of growth also suggests greater crystallinity of Hm compared to Gt.

Values of the MCS_a/MCS_c ratio (MCS_a = MCS₁₁₀ × 0.72; MCS_c = MCS₀₁₂ × 0.59) higher than the unit in all soils, except for LVA₁, indicate predominance of placoid morphology for Hm.

IS_{Hm} values ranged from 0.057 to 0.188 mol mol⁻¹ (Table 3). These results are lower than those observed for Gt, except in LVA₁. This reinforces the hypothesis that when these two minerals occur simultaneously in soils, Hm tends to be smaller than IS (Schwertmann et al., 1979; Schwertmann and Kämpf, 1985; Singh and Gilkes, 1992). Singh and Gilkes (1992), based on the linear regression coefficient adjusted between IS_{Gt} and IS_{Hm} (line slope = 0.5),

reported that Hm may accommodate approximately half of Al present in Gt in soils when these minerals coexist, which was also observed in this study (Figure 4b). However, the occurrence of IS_{Hm} values higher than half the values observed for Gt indicates that in soils with significant Hm contents, under favorable conditions, the occurrence of this phenomenon in Hm may be more effective.

In addition to the higher values of MCS_{Hm} , SSA_{Hm} values lower than those for Gt were observed, with few exceptions (LV_6 and LVA_1), in agreement with the results observed by Melo et al. (2001) and Carvalho Filho et al. (2015). The lack of correlation between IS_{Hm} and SSA_{Hm} , as well as between IS_{Hm} and MCS_{Hm012} , and MCS_{Hm104} and MCS_{Hm110} , show high variability of the factors involved in Hm crystallinity in the Oxisols studied.

In general, the MCS_{Mh} values were higher than those found for Hm and Gt, which reflects better crystallinity of Mh in soils derived from mafic rocks where their genesis is more associated with oxidation of magnetite inherited from the parent material (Curi and Franzmeier, 1987; Fontes and Weed, 1991; Costa et al., 1999). With values close to one, the MCS_{Mh220}/MCS_{Mh400} ratio indicates equal dimensions in the d_{220} and d_{400} directions of Mh.

IS_{Mh} values ranged from 0.033 to 0.194 mol mol⁻¹, similar to the values found by other authors in tropical and subtropical soils (Schwertmann and Fechter, 1984; Fontes and Weed, 1991; Costa et al., 1999; Carvalho Filho et al., 2015) and generally lower than those estimated for Hm and Gt. Thus, it can be suggested that in well-drained soils from mafic rocks, IS in Mh would occur throughout pedogenesis from its direct transformation after oxidation of magnetite inherited from the parent material.

The IS values estimated by mathematical equations of Schulze (1984), Schwertmann et al. (1979), and Schwertmann and Fechter (1984) for Gt (IS_{Gt}), Hm (IS_{Hm}), and Mh (IS_{Mh}), respectively, were not consistent with those obtained through chemical dissolution by CBD (IS_d). Correa et al. (2008) also did not observe correlation between the IS_{Gt} determined by

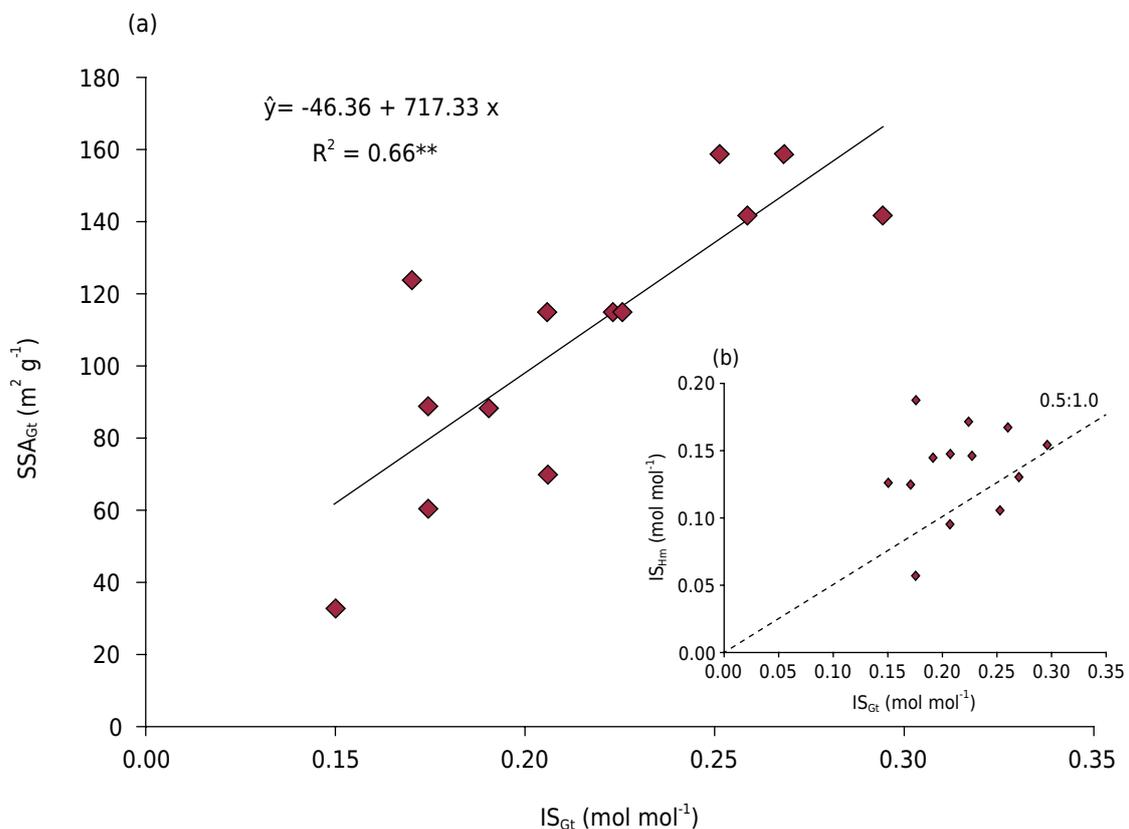


Figure 4. Relationship between specific surface area (SSA) and isomorphous substitution of Fe by Al (IS) values in Gt (a); and relationship between IS values in Hm and Gt (b). **: significant at 1 %.

chemical methods and that estimated by mathematical equations in soils of the Barreiras Group and, therefore, highlighted the need for studies to demonstrate the relationships between the crystallographic parameters of Gt and their chemical properties.

CONCLUSIONS

The occurrence of Mh contents higher than those of Hm and Gt in some Rhodic Oxisols underscores the importance of this mineral for soils originating from mafic rocks and suggests the need to reflect on the use of magnetic properties as criteria for taxonomic classification.

The estimate of Fe from Mh obtained for selective dissolution with 1.8 mol H₂SO₄ may not correspond to actual existence in the soil. In addition, the contents of Al extracted may be heavily influenced by other minerals that are sources of Al.

IS_{Gt} was higher than IS_{Hm} in all Rhodic Oxisols. This phenomenon has a strong influence on SSA_{Gt}; however, for Hm, other factors seem to exert a greater effect on crystallinity.

Hm crystals predominantly displayed a placoid shape in all Rhodic Oxisols and lower SSA_{Hm} in comparison to Gt crystals, which occurred both in the isodimensional and acicular forms.

The higher Mh crystallinity and IS_{Mh} values generally lower than those of Hm and Gt suggest that in well-drained soils originating from mafic rocks, the IS phenomenon in Mh seems to be a result of pedogenetic advances after its formation from magnetite oxidation.

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