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Maghemite quantification and magnetic signature of Brazilian soils with contrasting parent materials

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ABSTRACT

Maghemite (Mh) is a ferrimagnetic mineral that governs magnetism in the clay fraction, especially in well weathered soils from tropical and subtropical regions. In this work, we assessed different methods for Mh quantification [1: area of the reflections obtained by X-ray diffraction (XRD) (standard method); 2: Rietveld refinement; 3: selective dissolution with H_2SO_4 and; 4: magnetic susceptibility (χ)] by application to Brazilian soils with contrasting parent materials (itabirite, basalt, gabbro, tuffite, gneiss and amphibolite). The methods based on H_2SO_4 dissolution were found to overestimate the Mh content with respect to the standard method based on X-ray diffraction. This was particularly so with samples from gneiss and amphibolite and samples with higher contents in poorly crystalline Fe oxides. Mh contents based on magnetic susceptibility measurements or the XRD-Rietveld refinement were closer to those provided by the standard method. Mh was found to accumulate in well weathered soils and soils with a high Fe_2O_3 content. Exception were soils from tuffite, which had high Fe_2O_3 contents ($\sim$330 g kg^{-1}), exhibited low Mh levels ($\sim$5.5 g kg^{-1}). Irrespective of the parent material, Mh particles typically fall in a single domain magnetic behavior; however, they can also acquire multidomain characteristics, probably as a result of isomorphic substitution and aggregation with hematite.

1. Introduction

Maghemite (Mh) is a secondary Fe-oxide occurring mainly in tropical and subtropical soils (Schwertmann and Taylor, 1989; Bigham et al., 2002; Fink et al., 2016). Mh may be inherited from the parent material or formed by oxidation of lithogenic magnetite (Mt), among other pathways (Curi and Franzmeier, 1987; Fabris et al., 1995; Cornell and Schwertmann, 2003). In Brazil, Mh accounts for up to 40% of Fe-oxides in some soils from volcanic rocks (Costa et al., 1999) or up to 47% in soils from ferruginous dolomite rocks (Carvalho Filho et al., 2015).

Mh confers soils magnetic properties such as magnetic susceptibility (χ), coercivity (Hc) and remanent magnetization (Mr) (France and Oldfield, 2000; Long et al., 2015; Attoucheik et al., 2017). The magnetic properties of minerals are associated with the Fe content of their structure because this element contains incomplete 3d orbitals involved in electron transitions between orbitals that produce a magnetic moment (Thompson and Oldfield, 1986). Besides Mh, the clay fraction of soils contains other major Fe oxides such as hematite (Hm) and goethite (Gt), which are expected to have a low magnetic moment and are, thus, antiferromagnetic (France and Oldfield, 2000; Long et al., 2015).

The Fe-oxides Gt and Hm, which are typically present more frequently in soils than Mh, have traditionally been quantified by chemical analysis of dithionite–citrate–bicarbonate (DCB) extracts (Curi and Franzmeier, 1987; Costa et al., 1999; Carvalho Filho et al., 2015) or with physical techniques such as diffuse reflectance (Barrón and Torrent, 1986; Torrent and Barrón, 2008; Marques Jr. et al., 2014) or by X-ray diffraction (XRD). However, XRD reflection areas for Mh are difficult to determine because of the usually small amounts present in the clay fraction and of its strongest diffraction reflection (a d311-2.51–2.53 Å) coinciding with the Hm reflection (a d110–2.51 Å). One alternative method for Mh quantification is selective dissolution of Mh with H_2SO_4, which was initially proposed by Schwertmann and Fetcher (1984) and later modified by Costa et al. (1999); others are based on magnetic susceptibility (Costa et al., 1999) or on application of the Rietveld refinement to XRD data (Nonaka et al., 2017).

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Table 1
Localization of the Brazilian soils with their respective horizons, parent materials and climate.

Sample	Soil taxonomy[a]	Horizon	Parent material	Localization	Climate	T[b]	R[c]
						°C	mm
1-OX	Rhodic Hapludox	B	Itabirite	Nova Lima/MG	Cwb	18	1558
2-OX	Rhodic Hapludox	B	Basalt	Cascavel/PR	Cfa	19	1875
3-OX	Rhodic Hapludox	A	Basalt	Sananduva/RS	Cfb	17	1900
4-OX	Rhodic Hapludox	A	Basalt	Lagoa Vermelha/RS	Cfb	16	1939
5-MO	Typic Hapludoll	A	Basalt	Santa Cruz do Sul/RS	Cfa	18	1924
6-OX	Rhodic Hapludox	B	Basalt	Vargem Bonita/SC	Cfb	16	1760
7-OX	Rhodic Hapludox	B	Basalt	Água Doce/SC	Cfb	15	1724
8-OX	Rhodic Hapludox	B	Gabbro	Lavas/MG	Cwb	19	1621
9-OX	Rhodic Hapludox	B	Gabbro	Lavras/MG			
10-EN	Typic Hapludents	A	Gabbro	Lavras/MG			
11-EN	Typic Hapludents	A	Gabbro	Lavras/MG			
12-OX	Rhodic Hapludox	B	Tuffite	Patos de Minas/MG	Cwa	20	1448
13-MO	Typic Hapludoll	B	Tuffite	Patos de Minas/MG			
14-IN	Typic Dystrudepts	B	Tuffite	Patos de Minas/MG			
15-OX	Rhodic Hapludox	B	Gneiss	Nazareno/MG	Cwb	18	1689
16-UL	Rhodic Hapludult	B	Gneiss	Lavras/MG	Cwb	19	1621
17-OX	Rhodic Hapludox	B	Amphibolite	Miraí/MG	Cwa	20	1322
18-MO	Typic Hapludoll	B	Amphibolite	Italva/RJ	Aw	22	1163

[a] Soil Survey Staff, 2014.
[b] Mean annual temperature.
[c] Cumulative annual rainfall.

Mh content and magnetic susceptibility have been used in environmental studies on pedogenesis (Long et al., 2015) and in the characterization of paleoenvironments (Torrent et al., 2010; Wang et al., 2016), but also in soil mapping (Silva et al., 2016), soil fertility (Marques Jr et al., 2014; Siqueira et al., 2016), soil erosion (Rowntree et al., 2017) and even atmospheric pollution research (Grimley et al., 2017). However, different Mh quantification methods have led to also different or even controversial results that have precluded comparison. In this work, It was assessed various methods for quantifying Mh in soils and elucidated the properties of Mh from contrasting parent materials in Brazilian soils.

2. Material and methods

2.1. Samples and overall characterization

Samples from the A (0–20 cm) or B (80–100 cm) horizons of 18 soils were collected from different sites in Brazil (Table 1). The soils (Tables 1 and 2) spanned a wide range of Fe_2O_3 content from low (gneiss and amphibolite), to medium or high (gabbro, tuffite and basalt), and included iron-derived soils (itabirite) containing up to 71% Fe_2O_3, all measured by sulfuric digestion (Carvalho Filho et al., 2015). The variation of the parent material and the horizons sampled had the purpose of verifying that the methods could be used in a global way.

Soil samples were passed through 2 mm sieves (air-dried fine earth, ADFE) and subjected to the following determinations: grain-size fractionation with the modified pipette method (Baver et al., 1972; Gee and Bauder, 1986); total organic carbon (TOC) by oxidation with potassium dichromate in sulfuric acid (Donagema et al., 2011); and oxide content by sulfuric digestion (Donagema et al., 2011). The ratios between Fe, Al and Si oxides were used to calculate the molecular weathering indices *Ki* and *Kr* (Table 2).

2.2. Fe and Al dithionite and oxalate

After grain-size fractionation according to Jackson (1979), the clay fraction was subjected in triplicate to four successive extractions with dithionite–citrate–bicarbonate at 80 °C for Fe in pedogenic Fe-oxides (Fe_d) (Mehra and Jackson, 1960). Iron in poorly crystalline Fe-oxides (basically ferrihydrite) was determined with $0.2\,mol\,L^{-1}$ ammonium

oxalate at pH 3.0 in the dark (Fe_o) (McKeague and Day, 1966). The resulting suspensions were centrifuged at 3500 rpm for 10 min, and Fe and Al quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Varian 720-ES instrument.

2.3. Iron oxides

The concentrated Fe-oxides fraction were obtained by boiling the clay samples in $5\,mol\,L^{-1}$ NaOH (Kämpf and Shwertmann, 1982) to dissolve kaolinite and gibbsite, using sodium meta silicate pentahydrate to a $0.2\,mol\,L^{-1}$ concentration in the extractant to avoid dissolution and recrystallization of poorly crystalline, highly Al-substituted goethite (Kämpf and Schwertmann, 1982). After boiling in a sand bath for 1.5 h, the suspensions were centrifuged at 3500 rpm for 10 min and the supernatants discarded. Potentially formed artificial sodalite $[Na_4Al_3Si_3O_{12}\,(OH)]$ was removed by washing the residue with 90 mL of $0.5\,mol\,L^{-1}$ HCl twice (Norrish and Taylor, 1961). Also, excess salts in the final extract were removed by washing with 80 mL of $0.5\,mol\,L^{-1}$ $(NH_4)_2CO_3$ twice and then with 80 mL of deionized water. The residue was oven dried at 60 °C and gently milled for further analysis.

2.4. Maghemite quantification

2.4.1. X-ray diffraction and Rietveld refinement

The Fe oxide concentrates were analyzed by XRD (powder method) on a Bruker D8 Discover A25 diffractometer using a Ni filter and Cu α radiation (λ = 1.541838 Å). The X-ray tube, was operated at 60 mA and 50 kV, using a goniometer angular velocity of $0.4°2\theta\,min^{-1}$ and an amplitude of 10 to 67°2θ.

Initially, XRD was used to determine the proportions of Gt, Hm and Mh in the Fe-oxide concentrate from the area of (110) for Gt Eq. (1), (012) for Hm Eq. (2) (Schwertmann and Lathan, 1986) and (220) for Mh Eq. (3) (Costa et al., 1999) (see Table S1 in Supplementary material). The reflection areas for Hm and Mh were multiplied by a factor of 3.5 because they amounted to about 35% of that for the highest reflection. The total area was the combined area of Gt_{110}, $Hm_{012} \times 3.5$ and $Mh_{220} \times 3.5$.

$$Gt\% = \left(\frac{area\ 110}{total\ area} \right) \times 100 \qquad (1)$$