CRISTALLOCHEMICAL CHARACTERIZATION OF SYNTHETIC Zn-SUBSTITUTED MAGHEMITES (γ-Fe$_{2-x}$Zn$_x$O$_3$)[1]

Marcelo Augusto Batista[2], Antonio Carlos Saraiva da Costa[3], Ivan Granemann de Souza Junior[2] & Jerry Marshal Bigham[4]

SUMMARY

Maghemite (γ-Fe$_2$O$_3$) is the most usually found ferrimagnetic oxide in red basalt-derived soils. The variable degrees of ionic substitution of Fe^{3+} for different metals (e.g. Ti^{4+}, Al^{3+}, Mg^{2+}, Zn^{2+}, and Mn^{2+}) and non-metals in the maghemite structure influence some cristallochemical features of this iron oxide. In this study, synthetic Zn-substituted maghemites were prepared by co-precipitation in alkaline aqueous media of FeSO$_4$.7H$_2$O with increasing amounts of ZnSO$_4$.7H$_2$O to obtain the following sequence of Fe^{3+} for Zn^{2+} substitutions: 0.0, 0.025, 0.05, 0.10, 0.15, 0.20, and 0.30 mol mol^{-1}. The objective of this work was to evaluate the cristallochemical alterations of synthetic Zn-substituted maghemites. The dark black synthetic precipitated material was heated to 250 °C during 4 h forming a brownish maghemite that was characterized by chemical analysis as well as X ray diffraction (XRD), specific surface area and mass-specific magnetic susceptibility. The isomorphic substitution levels observed were of 0.0013, 0.0297, 0.0590, 0.1145, 0.1764, 0.2292 and 0.3404 mol mol^{-1}, with the formation of a series of maghemites from Fe$_2$Zn$_0$O$_3$ to Fe$_{(1.49)}$Zn$_{(0.770)}$)O$_3$. The increase in Fe^{3+} for Zn^{2+} substitution, [Zn mol mol^{-1}] increased the dimension a_0 of the cubic unit cells of the studied maghemites according to the regression equation: $a_{0=}0.8343 + 0.02591$Zn ($R^2 = 0.98$). On the other hand, the mean crystallite dimension and mass-specific magnetic susceptibility of the studied maghemites decreased with increasing isomorphic substitution.

Index terms: iron oxides, X ray diffraction, mass-specific magnetic susceptibility, specific surface area, isomorphic substitution.

RESUMO: *CARACTERIZAÇÃO CRISTALOQUÍMICA DE MAGHEMITAS SINTÉTICAS SUBSTITUÍDAS COM ZINCO (γ-Fe$_{2-x}$Zn$_x$O$_3$)*

A maghemita (γ-Fe$_2$O$_3$) é um óxido de Fe ferrimagnético comumente encontrado em solos Vermelho-Escuros derivados de rochas basálticas. Os graus variáveis de substituição isomórfica de Fe^{3+} por diferentes metais (por exemplo, Ti^{4+}, Al^{3+}, Mg^{2+}, Zn^{2+} e Mn^{2+}) e não-metais, na estrutura da maghemita, influenciam algumas características cristaloquímicas deste óxido de Fe. Maghemitas sintéticas substituídas com Zn foram preparadas por meio de co-precipitação em meio aquoso alcalino contendo FeSO$_4$.7H$_2$O e quantidades crescentes de ZnSO$_4$.7H$_2$O, para dar origem a uma contínua sucessão de substituição de Fe^{3+} por Zn^{2+}, nas seguintes proporções: 0,0, 0,025, 0,05, 0,10, 0,15, 0,20 e 0,30 mol mol^{-1}. O objetivo deste trabalho foi avaliar as alterações cristaloquímicas de maghemitas sintéticas substituídas com Zn. Após a síntese, o precipitado preto formado foi aquecido a 250 °C durante 4 h, formando uma maghemita de cor marrom, que foi caracterizada por análise química, difração de raios X (DRX), área superficial específica e suscetibilidade magnética. Os níveis de substituição isomórfica observados foram de 0,0013, 0,0297, 0,0590, 0,1145, 0,1764, 0.2292 e 0,3404 mol mol^{-1}, formando uma série de maghemitas de Fe$_2$Zn$_0$O$_3$ até Fe$_{1,49}$Zn$_{0,770}$O$_3$. O incremento da substituição de Fe^{3+} por Zn^{2+} [Zn mol mol^{-1}] aumentou a dimensão a$_0$ da cela unitária cúbica da maghemita, de acordo com a equação de regressão: a$_0$ = 0,8343 + 0,02591Zn (R^2 = 0,98). Por outro lado, o diâmetro médio do cristalito e a suscetibilidade magnética das maghemitas estudadas diminuíram com o aumento da substituição isomórfica.

Termos de indexação: óxidos de ferro, difração de raios X, suscetibilidade magnética, área superficial específica, substituição isomórfica.

INTRODUCTION

In humid subtropical and tropical conditions, the weathering of basic rocks with minerals such as olivine, pyroxene and plagioclase generally originate clayey soils with high Fe oxide content. These secondary oxides vary from amorphous to highly crystalline minerals and due to their abundance and diversity influence the physical and chemical soils properties considerably (Pombo et al., 1982). In the Brazilian Soil Classification System (Embrapa, 2006) Fe oxides are used at the third level (great group), to separate different taxonomic soil classes (a great part of these basaltic derived soils are classified as "Latossolos Vermelhos eutro or distro férricos").

Iron oxides are the most abundant metallic oxides in tropical soils (Schwertmann & Taylor, 1989). Maghemite and magnetite are mostly present in the clay and silt plus sand fractions, respectively, and are responsible for most of the magnetic behavior of different soils (Costa et al., 1999). Maghemite (γ-Fe$_2$O$_3$), the ferrimagnetic form of Fe$_2$O$_3$, is usually found in these soils, often concentrated in the topsoil (Schwertmann & Fechter, 1984). Maghemite formation is initiated by two basic processes: (a) oxidation of magnetite present in the coarse soil fraction (van der Marel, 1951; Murad & Schwertmann, 1993); and (b) burning of other Fe oxides in the presence of a C source at temperatures around 250 °C (Schwertmann & Taylor, 1989; Dearing, 1994).

Maghemite is derived from magnetite, since its cubic unit cell is easily inherited from the cubic inverse spinel structure of magnetite (Fasiska, 1967). Pure magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$) are rarely, if ever, found in nature. Isomorphic substitution of Fe for different elements is common, if not a rule, among these minerals. In soils, Al is mostly substituted by Fe in maghemite and mostly by Ti^{4+}, Mg^{2+}, Zn^{2+} and Mn^{2+} in primary magnetite (Schwertmann & Fechter, 1984; Sidhu et al., 1980), thus excluding maghemite formation from lithogenic magnetite, which generally contains little Al (Deer et al., 1962). It is also unlikely that the solution of a well-aerated, organic matter–poor soil would contain enough Fe^{2+} to react with Fe oxides to produce magnetite (Schwertmann & Taylor, 1989) and magnetostatic bacteria (Fassbinder et al., 1990).

Among all Fe-substituting elements, Al is the best documented. Iron for Al substitution was originally demonstrated in soil Fe oxides by chemical analysis and X ray diffraction (XRD) line shift (Norrish & Taylor, 1961). Since then, voluminous literature on aluminous Fe oxides appeared relative to the effect of this substitution on crystallographic and physico-chemical properties of Fe oxides and the use as an indicator of pedogenic processes. The existence and extent of Fe for Al isomorphic substitution has been indirectly investigated using the regression between the a_0 unit cell dimension and the degree of Al substitution [Al/(Fe + Al), mol mol^{-1}] (Vegard's law)

(Schulze, 1984; Schwertmann & Fechter, 1984; Schwertmann & Carlson, 1994), and also directly by chemical dissolution (Schwertmann, 1984). An impressive number of cations has been incorporated in synthetic Fe oxides besides Al: divalent Ni, Zn, Pb and Cd; trivalent Cr, Ga, V, Mn, Co, and Sc; and tetravalent Ge, and Si (Inoue et al., 1972; Stiers & Schwertmann, 1985; Cornell & Giovanoli, 1987; Ebinger & Schulze, 1989; Schwertmann et al., 1989; Cornell et al., 1992; Schwertmann & Pfab, 1994; Martin et al., 1997; Ford et al., 1997; Scheinost et al., 2000). Iron oxides such as magnetite and maghemite have been used to recover metals of polluted areas by co-precipitating the metals within their structure or by simple adsorption (Cornell & Schwertmann, 1996).

The Zn concentration in the earth's crust is around 70 mg kg^{-1} (Mason, 1971). The most heavily mined ores (sphalerite) tend to contain roughly 10 % Fe as well as 40–50 % Zn. Minerals from which zinc is extracted include sphalerite (ZnS), smithsonite ($ZnCO_3$), hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$], franklinite [(Zn, Fe, Mn)(Fe, Mn)$_2O_4$] and zincite (ZnO) (McPhail et al., 2003). Zinc is a common element in magnetite (Sidhu et al., 1980). In the weathering process of these primary minerals, the secondary Fe oxides formed (maghemite, hematite) might incorporate or inherit these elements in their crystalline structure. Magnetite (Fe_3O_4) and franklinite ($ZnFe_2O_4$) form a solid solution (Juillot, et al., 2003) between a ferrimagnetic and an antiferromagnetic mineral (Mullins, 1977; Ehrhardt et al., 2003). Maghemites containing Zn were observed by other authors (Gillot & Benloucif, 1992; Fukasawa et al., 1993). So far, just a few studies (e.g. Gillot & Benloucif, 1992) have analyzed the effect of continuous Zn incorporation into the maghemite structure and the influence on the crystallochemical properties of this ferrimagnetic oxide.

The objective of this study was to evaluate the cristallochemical alterations of synthetic Zn-substituted maghemites.

MATERIAL AND METHODS

Synthesis

The studied maghemites were obtained by the oxidation of precluding magnetites, synthesized by co-precipitation in aqueous KNO_3 alkaline solution, from $FeSO_4 \cdot 7H_2O$ with increasing amounts of $ZnSO_4 \cdot 7H_2O$ to promote isomorphic substitutions of 0.0, 0.025, 0.05, 0.10, 0.15, 0.20 and 0.30 mol mol^{-1} (Schwertmann & Cornell, 1991). Synthesis was performed in a N_2 atmosphere. After co-precipitation, a hand magnet easily and completely attracted the dark black material formed. This material was washed several times with distilled water to remove the salt excess, frozen and freeze-dried. Thereafter, this black

material was heated in a furnace in a free atmosphere to 250 °C for four hours producing a brownish powder, also attractable by a hand magnet.

Chemical analysis

Duplicates of the powder material (~100 mg) were put in glass tubes, plus 15 mL H_2SO_4 (20 % v/v), and placed in a digester block at a constant 350 °C until total dissolution. Solutions were stored and Zn and Fe contents determined by atomic absorption spectrophotometry. Expected and observed Zn^{2+} and Fe^{3+} relations were calculated based on the amount of Zn^{2+} and Fe^{3+} used in the synthesis and the values obtained in the total chemical analysis.

X ray diffraction (XRD)

The powdered material was XRD analyzed in a Shimadzu XRD 6000 diffractometer using CuKα radiation, in a step-scanning mode (0.02 °2θ/2 s) with approximately 5 % Si, added as internal standard for accurate determination of d-spacing values and line broadening. These patterns were exported to Grams® software to determine the areas, heights, positions, and full widths at half height (FWHH) of each diffraction line. The a_0 dimension of the cubic unit cell of maghemite was calculated from the six most intense diffraction lines: 220, 311, 400, 422, 511 and 440. The mean size of coherently diffracting domains (mean coherence length, MCL) along the a_0 axes of the diffraction lines were calculated using Scherrer's equation with a K value of 0.9 (Klug & Alexander, 1974).

Specific surface area (SSA)

The specific surface area was measured by BET (Brunauer et al., 1938) N_2 adsorption technique using a Quantachrome instrument (Model Nova 2000, USA).

Mass-specific magnetic susceptibility ($\varkappa_{LF}$) and frequency dependence of mass-specific magnetic susceptibility ($\varkappa_{FD}$)

Mass-specific magnetic susceptibility was determined in samples of the Zn-substituted maghemites using a Bartington MS2 magnetic susceptibility system coupled with a MS2B sensor (Dearing, 1994). This dual frequency meter exposes the sample to a weak alternating magnetic field of ~80 A m^{-1}. The MS2B sensor has both low (0.47 kHz) and high-frequency settings (4.7 kHz) for the identification of fine-grained paramagnetic or superparamagnetic materials. Powdered samples (10 cm^3) were weighed into 20 cm^3 plastic vials. The volumetric magnetic susceptibility (κ) was measured at both low and high-frequency settings, and the low-frequency mass susceptibility ($\varkappa_{LF}$) was calculated as follows (Dearing, 1994): $\varkappa_{LF} = (10 \kappa_{LF}/m)$, where m is the mass (g).

The presence of superparamagnetic minerals with very small particle size (< 0.03 μm) was determined from the difference in κ measured at low and high frequency settings and was expressed as the percentage dual frequency magnetic susceptibility (Dearing, 1994): χ_{FD} % = [(κ_{LF}–κ_{HF}/κ_{LF}) x 100].

RESULTS AND DISCUSSION

Chemical analysis

The values of Zn^{2+} and Fe^{3+} relationship observed in synthetic maghemites were close to the expected values (Table 1), with a coefficient of variation below 2 %.

XRD identification of maghemite

Figure 1 shows the X ray powder diffraction patterns obtained for the seven synthetic products. For all samples, only maghemite diffraction lines were observed. Initially, 21 diffraction lines were identified

for pure maghemite ($Fe_2Zn_0O_3$). With Fe substitution for Zn in the crystal structure, only 11 diffraction lines were observed and six with strong intensities (220, 311, 400, 422, 511 and 440) were used for further crystallographic characterization. The reduction of the amount of the diffraction lines among the Zn substituted maghemites suggests that this metal induced some disorder in the crystals as observed by Da Costa et al. (1998). The fairly large number of diffraction lines in pure maghemite, which generally presents poor or very poor intensities, occurs because the oxidation of the maghemite precursor ejects 11 % of the Fe^{2+} from the structure, thereby creating vacancies. Some superstructure lines are clearly visible, indicating an ordered arrangement of the vacancies on B sites (Haneda & Morrish, 1977; Da Costa et al., 1994). Where the vacancies are ordered, superstructure diffraction lines appear in the XRD pattern and a tetragonal structure can be indexed (Schwertmann & Cornell, 1991). Gillot & Benloucif (1992) also observed a fairly large number of diffraction lines with poor or very poor intensities in Zn-substituted maghemites.

Table 1. Values of expected and observed Zn^{2+} and Fe^{3+} contents of the synthetic maghemites

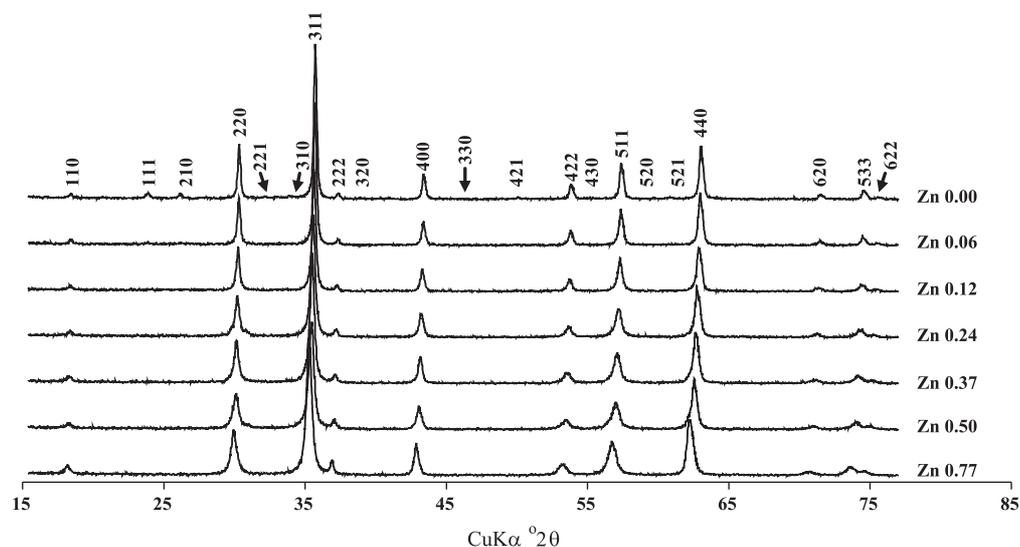| Zn/Fe expected ratio	Zn/Fe observed ratio	Isomorphic substitution	Chemical formula $Fe_{2-x}Zn_xO_3$
		$mol\ mol^{-1}$	$mol_c\ mol_c^{-1}$
0.0000	0.0000	0.0013	$Fe_{(2.00)}Zn_{(0.000)}O_3$
0.0300	0.0306	0.0297	$Fe_{(1.96)}Zn_{(0.060)}O_3$
0.0616	0.0627	0.0590	$Fe_{(1.92)}Zn_{(0.120)}O_3$
0.1301	0.1293	0.1145	$Fe_{(1.84)}Zn_{(0.240)}O_3$
0.2065	0.2142	0.1764	$Fe_{(1.75)}Zn_{(0.370)}O_3$
0.2927	0.2974	0.2292	$Fe_{(1.67)}Zn_{(0.500)}O_3$
0.5016	0.5161	0.3404	$Fe_{(1.49)}Zn_{(0.770)}O_3$

Figure 1. Powder XRD patterns of synthetic maghemites with different zinc isomorphic substitution levels.

The relative intensity ratios (I_{hkl}/I_{311}) of the XRD intensities related to maghemite diffraction planes 220, 400, 422, 511 and 440 by the most intense one (311) were differently affected by the degree of Zn substitution. The relative intensities for the planes 400 and 440 increased as Zn ion substitution increased, according to the regression equation: $I_{400}/I_{311} = 17.4270 + 0.2029Zn$ ($R^2 = 0.9146$) and $I_{440}/I_{311} = 37.2980 + 0.3033Zn$ ($R^2 = 0.8511$), respectively. On the other hand, plane 220 decreased as Zn ion substitution increased, according to the regression equation $I_{220}/I_{311} = 32.434-10.091 Zn$) ($R^2 = 0.7511$). Other planes (422 and 511) showed no tendency with increasing Zn ion substitution. Working with $Ni_{0,2}Zn_xMg_{0.8-x}Fe_2O_4$ ferrites, Amer & El Hiti (2001) also observed increasing relative intensities for planes 220 and 422 as Zn ion substitution increased.

The increasing Zn/Fe substitution is possible because Fe and Zn have similar ionic radii. For isomorphic substitution, the atom or ion size is the decisive factor while it is not essential that the ions have the same charge or valence, since electric neutrality is maintained in the crystal structure (Mason, 1971; Schulze, 1989).

Figure 2 shows that the diffraction lines 422, 511 and 440 moved considerably to lower 2θ angles indicating increase of the a_0 unit cell parameter. This behavior was also observed for all the six most intense diffraction lines. This is possible because Fe^{3+} has smaller radii size (r = 0.064 nm) than Zn^{2+} (r = 0.074 nm). Contrastingly, Schwertmann & Fechter (1984) observed that maghemites from highly weathered soils with a high degree of Fe substitution for Al had significantly lower unit cell dimensions than
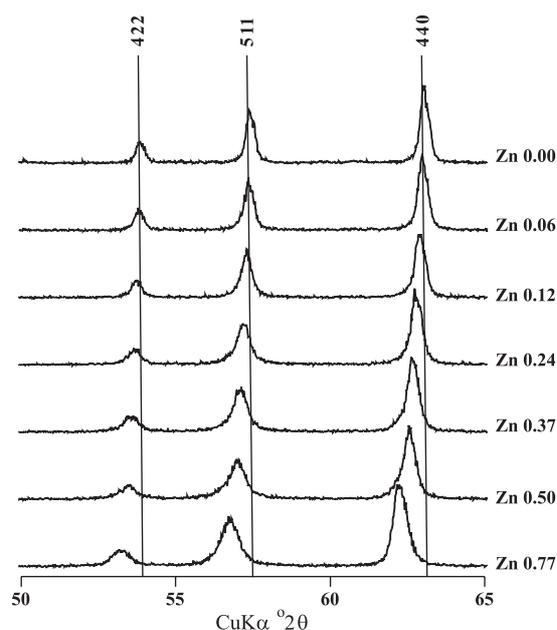
pure maghemites because Al^{3+} (r = 0.053 nm) has a smaller radii size than Fe^{3+}.

The measurement of the full width at half height (FWHH) of diffraction lines enables one to estimate the order degree and mean crystallite dimension of minerals (Resende et al., 2005). In this study, the increasing percentage of Zn for Fe substitution increased the FWHH values (Figure 2) of all six diffraction lines evaluated and therefore decreases mean crystallite dimension (MCD) and order degree of the synthetic minerals, according to the regression equation MCD (nm) = $71.3900 – 166.42Zn$ ($R^2 = 0.65$) (Figure 3).

On the other hand, the partial presence of Zn in the place of Fe in maghemite increased the d spacing values. Cornell & Schwertmann (1996) observed decrease in d space with increasing substitution of Al for Fe in goethites, where d is the distance of plane separation.

The unit cell size diameter (a_0) (Figure 4) increased with increasing Zn^{2+} content within maghemites. For pure maghemite the a_0 observed was 0.8343 nm, close to the a_0 value of the Joint Committee on Powder Diffraction Standards (JCPDS) card # 39–1.346, which is 0.8351. As observed previously, when isomorphic substitution occurs for a larger ion, a_0 increases the unit cell diameter. An opposite trend was observed by Schwetmann & Fechter (1984) where isomorphic substitution of Fe for Al decreased the unit cell size, due to the smaller radii in Al^{3+} than in Fe^{3+}.

In the linear regression equation fitted (Figure 4) to relate a_0 to the Zn^{2+} isomorphic substitution degree the value for the coefficient of determination was high ($R^2 \approx 0.98$). In this case a_0 values can be calculated using XRD data from any one of the six most intense diffraction lines by means of the following $a_0 = (\lambda/2) [(h^2 + k^2 + l^2)^{1/2}/sin\theta)]$ equation (Klug & Alexander, 1974) where λ is wavelength, hkl is the Miller index and θ the angle of incidence. There was a significant negative interaction between mass-specific magnetic

Figure 2. Details of the reflexes 422, 511 and 440 of synthetic maghemites with different zinc isomorphic substitution levels.
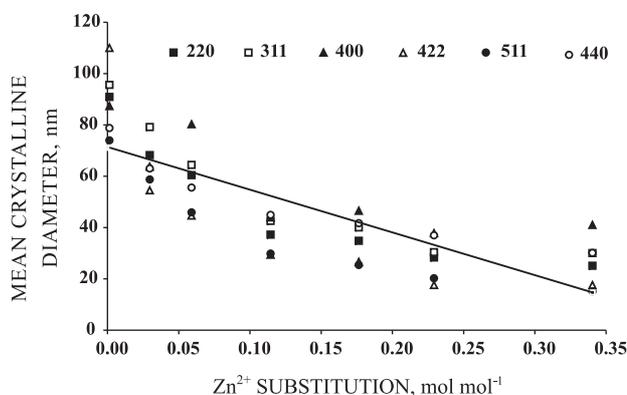

Figure 3. Mean crystallite dimension (MCD) of synthetic maghemites with different Fe^{3+} for Zn^{2+} substitution degrees.

susceptibility ($\varkappa_{LF}$) and the degree of isomorphic substitution of Fe for Zn (Figure 5). This was due to the inclusion of a diamagnetic element (Zn) in the crystal structure of maghemite, which reduced the magnetic moment of the mineral (Dearing et al., 1996). The $\varkappa_{LF}$ values of pure maghemite was 49,726 10^{-8} m^3 kg^{-1} decreasing to 32,472 10^{-8} m^3 kg^{-1} at the level 0.3404 mol mol^{-1} of Zn. The XRD data (Figures 1 to 4) and the steady decrease of the $\varkappa_{LF}$ values (Figure 5) confirm the existence of a continuous solid solution for the range of Zn for Fe substitution evaluated. Working with maghemites formed from phosphate ferrihydrite, Barrón & Torrent (2002) observed that with an increasing P/Fe ratio, the values of $\varkappa_{FD}$ increased abruptly to of maximum of 24,000 x 10^{-8} m^3 kg^{-1} at P/Fe ≈ 0.0275, to finally drop to < 2,000 x 10^{-8} m^3 kg^{-1} at P/Fe = 0.06. Magnetic susceptibility values for maghemite (Dearing, 1994) were reported from 44,000 10^{-8} to 111,600 10^{-8} m^3 kg^{-1}. Costa et al. (1999) observed values of around 91,000 10^{-8} m^3 kg^{-1} in soil maghemites.

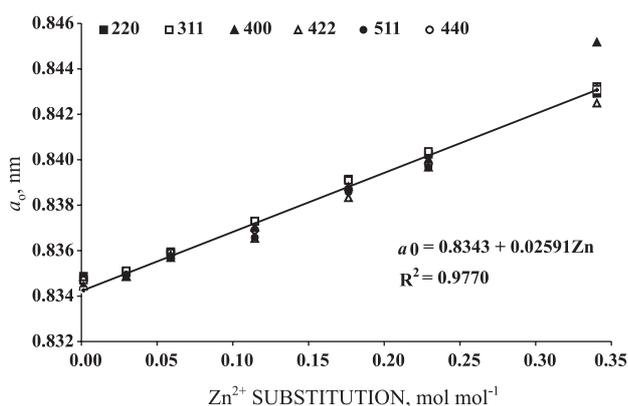The synthesized mineral is maghemite, a ferromagnetic mineral that decreases $\varkappa_{FD}$ due to the inclusion of a diamagnetic element (Zn) in the crystal structure (Dearing et al., 1996), which reduces the magnetic moment of the mineral. Higher values of Zn for Fe substitution might be possible and will be subject of further studies.

Frequency dependence values of the mass-specific magnetic susceptibility ($\varkappa_{FD}$) for the Zn-substituted maghemites varied from 1.5 to 7.5 % (Figure 6). According to Dearing (1994), from pure maghemite to maghemite with approximately 0.1435 mol mol^{-1} Zn of isomorphic substitution ($\varkappa_{FD}$ < 2), less than 10 % of the sample has superparamagnetic behavior. Zn-substituted maghemites with isomorphic substitution above 0.1435 mol mol^{-1} are admixtures of (super-) paramagnetic and coarser stable single domain and multidomain grains.

Increasing Zn for Fe isomorphic substitution decreased the MCD with increasing $\varkappa_{FD}$, in other words, as particle size or coherent domain decreases, superparamagnetic behavior predominates (Costa et al., 1999; Dearing, 1994) (Figures 3 and 6)

Costa et al. (1999) observed $\varkappa_{FD}$ values ranging from 10–18 % in the clay to 0–10 % for the sand and silt fractions of basalt-derived soils. The authors attributed the higher $\varkappa_{FD}$ values to the predominance of superparamagnetic secondary maghemite in the clay size fraction of the soils. The lowest $\varkappa_{FD}$ values were observed in the sand and silt fraction where coarse, single or multidomain magnetites or maghemites prevail.

The specific surface area (SSA) of the synthetic maghemite increased linearly as Fe for Zn substitution increased (Figure 7). Increasing SSA values agree with the decrease of the MCD (Figure 3). The substitution of Fe for Zn atoms within the crystal structure of synthetic maghemites hampers crystal growth on all faces of the cubic structure. For most Fe oxides, the presence of exotic chemical elements reduces the crystal size, enhances the specific surface area and decreases the mean crystalline diameter (Cornel & Schwertmann, 1996). Contrastingly, Sidhu

Figure 4. Relationship between the a_o unit cell dimension of maghemites and Fe^{3+} for Zn^{2+} substitution.
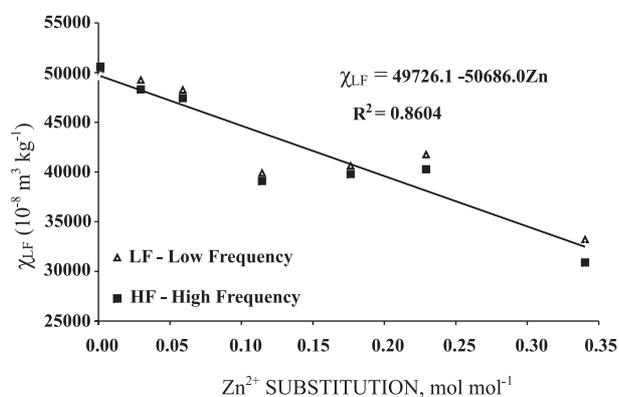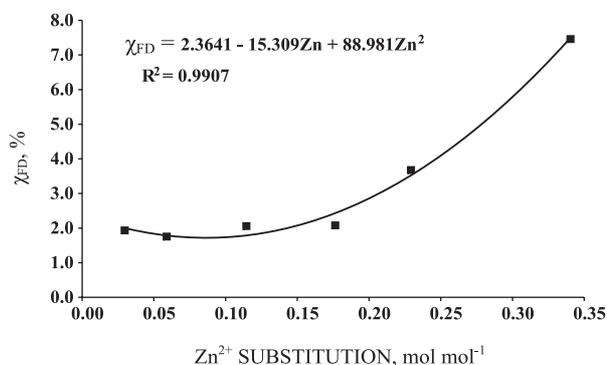
$a_0 = 0.8343 + 0.02591 Zn$
$R^2 = 0.9770$

Figure 5. Mass-specific magnetic susceptibility ($\varkappa_{LF}$) of synthetic maghemites with different zinc isomorphic substitution degrees.

$\chi_{LF} = 49726.1 - 50686.0 Zn$
$R^2 = 0.8604$

Figure 6. Frequency dependence of the mass-specific magnetic susceptibility ($\varkappa_{FD}$) of synthetic maghemites with different zinc isomorphic substitution degrees.

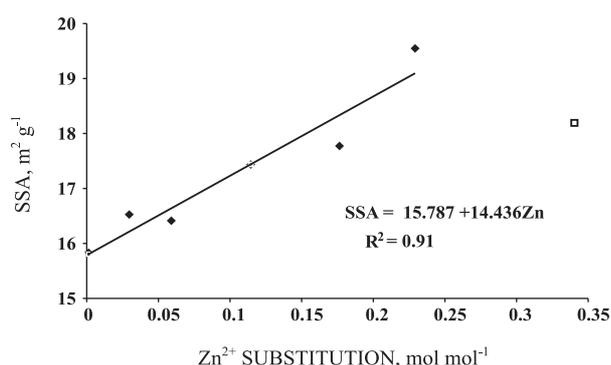$\chi_{FD} = 2.3641 - 15.309 Zn + 88.981 Zn^2$
$R^2 = 0.9907$

Figure 7. Specific surface area (SSA) of synthetic maghemites with different zinc isomorphic substitution degrees. (▫) Outlier, not considered in regression.

(1988) observed maghemites without Zn with a mean SSA value of 10.3 m^2 g^{-1}, a value below the intercept ($\approx$ 15.8 m^2 g^{-1}) in figure 7. The same author observed no relation between Zn substitution levels and SSA values. The increase in surface specific area is considered to be related to the decrease in maghemite crystallite size with increasing Zn-substitution (Figure 3).

CONCLUSIONS

1. The synthesized maghemites achieved high degrees of Fe^{3+} for Zn^{2+} substitution (maximum of 0.3404 mol mol^{-1}).

2. The values of d-spacing, MCD and χ_{LF} decreased with increasing degrees of Fe^{3+} for Zn^{2+} substitution in the studied maghemites.

3. Both a_0 unit cell dimension and SSA increased with increasing degrees of Fe^{3+} for Zn^{2+} substitution in the studied maghemites.

ACKNOWLEDGMENTS

LITERATURE CITED

AMER, M.A. & EL HITI, M. Mössbauer and X ray studies for $Ni_{0.2}Zn_xMg_{0.8-x}Fe_2O_4$ ferrites. J. Magnet. Magnetic Mater., 234:118-125, 2001.

BARRÓN, V. & TORRENT, J. Evidence for a simple pathway to maghemite in Earth and Mars soils. Geochim. Cosmochim. Acta, 66:2801-2806, 2002.

BRUNAUER, S.; EMMETT, P.P. & TELLER, E. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc., 60:309-319, 1938.

CORNELL, R.M. & GIOVANOLI, R. Effect of manganese on the transformation of ferrihydrite into goethite in alkaline media. Clays Clay Miner., 35:11-20, 1987.

CORNELL, R.M. & SCHWERTMANN, U. The iron oxides: Structure, properties, reactions, occurrence, and uses. Weinheim, Wiley VCH, 1996. 664p.

CORNELL, R.M.; GIOVANOLI, R. & SCHNEIDER, W. The effect of nickel on the conversion of amorphous iron(III) hydroxide into more crystalline iron oxides in alkaline media. J. Chem. Technol. Biotechnol., 53:73-79, 1992.

COSTA, A.C.S.; BIGHAM, J.M.; RHOTON, F.E. & TRAINA, S.J. Quantification and characterization of maghemite in soils derived from volcanic rocks in Southern Brazil. Clays Clay Miner., 47:466-473, 1999.

DA COSTA, G.M.; DE GRAVE, E. & VANDENBERGHE, R.E. Mössbauer studies of magnetite and Al-substituted maghemites. Hyperfine Interact., 117:207-243, 1998.

DA COSTA, G.M.; DE GRAVE, E.; BOWEN, L.H.; VANDENBERGHE, R.E. & DE BAKKER, P.M.A. The center shift in Mössbauer spectra of maghemite and aluminum maghemites. Clays Clays Miner., 42:628-633, 1994.

DEARING, J. Environmental magnetic susceptibility. Using the Bartington MS2 system. Kenilworth, Chi Publ., 1994.

DEARING, J.A.; HAY, K.L.; BABAN, S.M.J.; HUDDLESTON, A.S.; WELLINGTON, E.M.H. & LOVELAND, P.J. Magnetic susceptibility of soil: An evaluation of conflicting theories using a national data set. Geophys. J. Int., 127:728-734, 1996.

DEER, W.A.; HOWIE, R.A. & ZUSSMAN, J. Rock-forming minerals - Non silicates. New York, Willy & Sons, 1962. v.5. 371p.

EBINGER, M.H. & SCHULZE, D.G. Mn-substituted goethite and Fe-substituted groutite synthesized at acid pH. Clays Clay Miner., 37:151-156, 1989.

EHRHARDT, H.; CAMPBELL, S.J. & HOFMANN, M. Magnetism of the nanostructured spinel zinc ferrite. Script. Mater., 48:1141-1146, 2003.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA - EMBRAPA. Sistema brasileiro de classificação de solos. 2.ed. Brasília, Embrapa Produção de Informação, Rio de Janeiro, Embrapa Solos, 2006. 306p.

FASISKA, E.J. Structural aspects of the oxides and oxidehydrates of iron. Corrosion Sci., 7:833-839, 1967.

FASSBINDER, J.W.E.; STANJEK, H. & VALI, H. Occurrence of magnetic bacteria in soil. Nature, 343:161-163, 1990.

FORD, R.G.; BERTSCH, P.M. & FARLEY, K.J. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. Environ. Sci. Technol., 31:2028-2033, 1997.

FUKASAWA, T.; IWATSUKI, M. & FURUKAWA, M. State analysis and relationship between lattice constants and compositions including minor elements of synthetic magnetite and maghemite. Anal. Chim. Acta, 281:413-419, 1993.

GILLOT, B. & BENLOUCIF, R.M. X ray diffraction, IR spectrometry and high resolution electron microscopy on ordered zinc-substituted maghemites. Mater. Chem. Phys., 32:37-41, 1992.

HANEDA, K. & MORRISH, A.H. Structural peculiarities in magnetic small particles. Nuclear Instr. Meth. Physics Res., B76:132-137, 1977.

INOUE, K.; ISHII, S.; KANEKO, K. & ISHIKAWA, T. The effect of copper (II) on the crystallization of a Fe-OOH. Z. Anorg. Allg. Chemic, 391:86-96, 1972.

JUILLOT, F.; MORIN, G.; ILDEFONSE, P.; TRAINOR, T.P.; BENEDETTI, M.; GALOISY, L.; CALAS, G. & BROWN, JR, G.E. Occurrence of Zn/Al hydrotalcite in smelter-impacted soils from Northern France: Evidence from EXAFS spectroscopy and chemical extractions. Am. Miner., 88:509-526, 2003.

KLUG, H.P. & ALEXANDER, L.E. X ray diffraction procedures for polycrystalline and amorphous materials. 2.ed. New York, Wiley, 1974. 966p.

MARTIN, F.; ILDEFONSE, P.; HAZEMANN, J.L.; MATHE. P.E.; NOACK, Y.; GRAUBY, O. BEZIAT, D. & DE PARSEVAL, P. Gallium crystal chemistry in synthetic goethites. J. Phys., 4 : 821-822, 1997.

MASON, B. Princípios de geoquímica. São Paulo, Polígono, 1971. 381p.

McPHAIL, D.C.; SUMMERHAYES, E.; WELCH, S. & BRUGGER, J. The geochemistry and mobility of zinc in the regolith. In: ROACH, I.C., ed. Advances in regolith, Canberra, CRC, 2003. p.287-291.

MULLINS, C.E. Magnetic susceptibility of the soil and its significance in soil science – A review. J. Soil Sci., 28:223-246, 1977.

MURAD, E. & SCHWERTMANN, U. Temporal stability of a finegrained magnetite. Clays Clay Miner., 41:111-113, 1993.

NORRISH, K. & TAYLOR, R.M. The isomorphous replacement of iron by aluminium in soil goethites. Eur. J. Soil Sci., 12:294-306, 1961.

POMBO, L.C.A.; KLAMT, E.; KUNRATH, L. & GIANLUPPI, D. Identificação de óxidos de ferro na fração argila de Latossolo Roxo. R. Bras. Ci. Solo, 6:13-17, 1982.

RESENDE, M.; CURI, N.; KER, C.J. & REZENDE, S.B. Mineralogia de solos brasileiros: Interpretação e aplicações. Lavras, Universidade Federal de Lavras, 2005. 192p.

SCHEINOST, A.C.; STANJEK, H.; SCHULZE, D.G.; GASSER, U. & SPARKS, D.L. Structural environment and oxidation state of Mn in goethite-groutite solid-solutions. Am. Miner., 86:139-146, 2000.

SCHULZE, D.G. The influence of aluminum on iron oxides: VIII. Unit-cell dimensions of Al-substituted goethites and estimation of Al from them. Clays Clay Miner., 32:36-44, 1984.

SCHULZE, D.G. An introduction to soil mineralogy. In: DIXON, J.B. & WEED, S.B., eds.. Minerals in soil environments. Madison, Soil Science Society of America, 1989. p.1-34.

SCHWERTMANN, U. The influence of aluminium on iron oxides: IX. Dissolution of Al-goethites in 6M HCl. Clay Miner., 19:9-19, 1984.

SCHWERTMANN, U. & CARLSON, L. Aluminium influence on iron oxides: XVII. Unit-cell parameters and aluminium substitution of natural goethites. Soil Sci. Soc. Am. J., 58:256-261, 1994.

SCHWERTMANN, U. & CORNELL, R.M. Iron oxides in the laboratory - Preparation and characterization. Weinheim, Verlagsgesellschaft, 1991. 137p.

SCHWERTMANN, U. & FECHTER, H. The influence of aluminium on iron oxides. XI. Aluminium substituted maghemite in soils and its formation. Soil Sci. Soc. Am. J., 48:1462-1463, 1984.

SCHWERTMANN, U. & PFAB, G. Structural vanadium in synthetic goethites. Geochim. Cosmochim. Acta, 58:4349-4352, 1994.

SCHWERTMANN, U. & TAYLOR, R.M. Iron oxides. In: DIXON, J.B. & WEED, S.B., eds.. Minerals in soil environments. 2.ed. Madison, Soil Science Society of America, 1989. p.379-438.

SCHWERTMANN, U.; GASSER, U. & STICHER, H. Chromium-for-iron substitution in synthetic goethites. Geochim. Cosmochim. Acta, 53:1293-1297, 1989.

SIDHU, P.S. Transformation of trance element substituted maghemite to hematite. Clays Clay Miner., 36:31-38, 1988.

SIDHU, P.S.; GILKES, R.J. & POSNER, A.M. The behavior of Co, Ni, Zn, Cu, Mn and Cr in magnetites during alteration to maghemite and hematite. Soil Sci. Am. J., 44:135-138, 1980.

STIERS, W. & SCHWERTMANN, U. Evidence for manganese substitution in synthetic goethite. Geochim. Cosmochim. Acta, 49:1909-1911, 1985.

van der MAREL, H.W. g-Ferric oxide in sediments. J. Sedim. Petrol., 21:12-21, 1951.