

MAGNETITE AND ITS TRANSFORMATION TO HEMATITE IN A SOIL DERIVED FROM STEATITE⁽¹⁾

G. P. SANTANA⁽²⁾, J. D. FABRIS⁽³⁾, A. T. GOULART⁽⁴⁾ & D. P. SANTANA⁽⁵⁾

SUMMARY

The main objective of this work was to characterize the magnetic minerals and to identify their pedogenic transformation on a steatite-forming soil of Minas Gerais, Brazil. The iron-rich spinel phase was characterized by chemical analysis, powder X-ray diffraction, Mössbauer spectroscopy, with and without an externally applied magnetic field of 6 tesla, and saturation magnetization measurements. Nearly stoichiometric and well-crystallized magnetite was the only magnetic mineral actually detected. The cubic unit cell parameter of the fresh rock magnetite was found to be $a_0 = 0.8407(5)$ nm. Hematite (hexagonal cell; $a = 0.5036(3)$ nm, $c = 1.375(4)$ nm) was detected in the altered rock and in the sand-soil and silt-soil fractions. Magnetite is assumed to transform into hematite during pedogenesis through progressive oxidation of structural Fe^{2+} to Fe^{3+} . In partially oxidized magnetites, a relatively small proportion of Fe^{3+} was interpreted as being uncoupled from the Fe^{2+} - Fe^{3+} charge transfer system, in octahedral sites of the spinel structure. Compositional formulae of magnetite with different degrees of non-stoichiometry are proposed. Ilmenite was found in minor proportions in the magnetically extracted portions from both rock and soil samples.

Index terms: Iron-rich spinel, iron oxide, soapstone, magnetic soil, Mössbauer spectroscopy.

⁽¹⁾ This work is part of the thesis of the first author, presented to the Departamento de Química of the Universidade Federal de Minas Gerais, Brazil, as a partial requirement to obtain the title of Doctor in Science - Chemistry. It was originally planned and supervised by the late Professor Milton Francisco de Jesus Filho.

⁽²⁾ Associate Professor, Departamento de Química, Universidade do Amazonas - UA. CEP 69077-000 Manaus (AM).

⁽³⁾ Professor of Chemistry, Departamento de Química, Universidade Federal de Minas Gerais - UFMG. CEP 31270-901 Belo Horizonte (MG), Brazil.

⁽⁴⁾ Associate Professor (presently, retired), Departamento de Química, Universidade Federal de Viçosa - UFV. CEP 36571-000 Viçosa (MG).

⁽⁵⁾ Researcher, EMBRAPA/CNPMS, Caixa Postal 151, CEP 35701-970 Sete Lagoas (MG).

RESUMO: *MAGNETITA E SUA TRANSFORMAÇÃO PARA HEMATITA EM UM SOLO DERIVADO DE ESTEATITO*

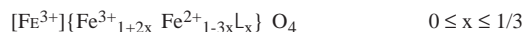
O presente trabalho objetivou caracterizar o mineral magnético e identificar suas rotas pedogenéticas de transformação em um solo formado sobre esteatito, de Minas Gerais, Brasil. O óxido de ferro isoestrutural ao espinélio foi identificado e caracterizado por análises químicas, difração de raios X, espectroscopia Mössbauer e medidas de magnetização de saturação. Na rocha fresca, foi encontrada magnetita estequiométrica e bem cristalizada, com parâmetro da rede cúbica, $a_0 = 0.8407(5)$ nm. Nas frações areia e silte, foram detectadas magnetita parcialmente alterada e hematita estequiométrica e bem cristalizada, com parâmetros da rede hexagonal, $a = 0.5036(3)$ nm e $c = 1.375(4)$ nm. A ocorrência dessas hematitas deveu-se principalmente à oxidação do Fe^{2+} a Fe^{3+} , no sítio octaédrico da magnetita, durante a pedogênese. Esse processo foi caracterizado pelo aparecimento de pequena quantidade de Fe^{3+} eletronicamente desacoplada, encontrada nas magnetitas parcialmente oxidadas, cujas fórmulas para as diferentes estequiometrias foram propostas. Verificou-se também pequena quantidade de ilmenita nas amostras de rocha e de solo.

Termos de indexação: Espinélios ricos em ferro, óxido de ferro, pedra-sabão, solo magnético, espectroscopia Mössbauer.

INTRODUCTION

Soils containing iron-rich spinel phases, commonly magnetite (ideal formula, Fe_3O_4) or maghemite (γFe_2O_3), both ferrimagnetically ordered oxides with spinel structure, that impart a soil magnetization higher than $1 J T^{-1} kg^{-1}$ ($\equiv A m^2 kg^{-1}$), are considered magnetic. In a recent paper, Fontes et al. (2000) discussed several mineralogical aspects and reported magnetic measurements on samples of soils from five different lithodomains. Magnetic pedons cover as much as 5% of the Brazilian land area (Resende et al., 1986; Moukarika et al., 1991; Fabris et al., 1997a). Most commonly, iron oxides in such intensively weathered soils bear significant amounts of isomorphic substituents, such as Al^{3+} , Ti^{4+} , and Mg^{2+} . Magnetite has been earlier reported as being the main iron-rich spinel in the sand fraction, whereas maghemite would more likely be found in the finer fractions of magnetic soils forming on mafic lithology (CSESP, 1960; Rauen, 1980; Curi 1983; Santana, 1984; Curi & Franzmeier 1987; Resende et al. 1988; Demattê & Marconi 1991). Other works have unequivocally detected only maghemite in the soil-sand fraction (Allan et al., 1989; Fabris et al., 1995; Goulart, 1998), in the transitional C/R horizon (Ferreira, 1995), or even in the slightly altered parent rock (Pinto et al., 1997; Pinto et al., 1998) of tropical mafic systems. Magnetite is most probably the lithogenic precursor of this soil maghemite in such systems (Jesus Filho et al., 1995; Fabris et al., 1997b; Mussel et al., 1999). Still recently, magnetite was identified in the sand fraction of a basalt-derived soil from a subtropical area of north Argentine (Mijovilovich et al., 1998). Those results

may suggest that the stability of the rock-magnetite is somehow related to the climate and is significantly sensitive to the intense weathering conditions prevailing during pedogenesis in tropical environments. As a corollary, a general iron oxide transformation pathway, starting on magnetite would involve the following fundamental steps, in mafic systems: magnetite (fresh rock) $\xrightarrow{(1)}$ maghemite (altered rock and soil) $\xrightarrow{(2)}$ hematite (soil). Basalt magnetite is progressively oxidized to soil maghemite, which is finally transformed to hematite. Step (1) is a relatively fast process in that lithology and is accomplished by progressive oxidation of octahedral $\{Fe^{2+}\}$ to $\{Fe^{3+}\}$, by losing some structural iron and creating cation vacancies, to compensate unbalanced charges, according to the following substitutional series



where [] and { } stand for tetrahedral and octahedral sites and L represents cation vacancies in the spinel structure, respectively; in step (2), much of certain substitutional elements (Co, Ni, Zn and Cu) tend to migrate from the lattice toward the surface of the grain whereas Mn and Cr are favourably retained in the hematite structure (Sidhu et al., 1980). Al-hematite and Al-goethite are ubiquitously found in pedoenvironments (e.g. Bigham et al., 1978; Schwertmann & Taylor, 1989). An important question arises from those observations: would this mineralogenic chain be still valid for other lithologies than those dominated by basalt-like rocks, where titanium is typically the main substituent for iron in the lithogenic magnetite?

Soils forming on steatite are also magnetic, but differently of those from mafic lithology, the magnetization is thought to be essentially due to the presence of magnetite inherited from this metasomatic ultramafic/ultrabasic rock, which also contains talc, dolomite and magnesian chlorite as major minerals (Roeser et al., 1980; Ladeira et al., 1983; Roeser et al., 1987). Gonçalves et al. (1991) described a steatite ("soapstone") from Congonhas, MG, Brazil, as having talc (57.5%), carbonate (29.1%), chlorite (8.4%), tremolite (1.4%) and an opaque fraction (3.6%). However, no further study regarding the nature of the magnetite from steatite and its transformation during pedogenesis in this lithology has been reported.

So far, it is not clear if or how the pedogenic stability of lithogenic magnetite is related to the nature of the parent material. However, the factors affecting its formation in the rock or those prevailing during pedogenesis determine its fate through soil mineral genesis pathways. Redox potential, pH and ions (Fe^{3+} , for example), organic matter and water availability are among possible factors that govern the geochemical processes.

Very commonly, the magnetic iron oxide fraction in soils corresponds to a range of solid solution between Fe_3O_4 and $\gamma\text{Fe}_2\text{O}_3$, which means that a separation of the two phases may not be possible in practice (Coe et al., 1971).

Selective chemical dissolution during sample preparation may improve substantially the mineralogical analysis of iron oxide in complex soil mineral assemblages. Concentrated NaOH preferentially removes silicate and gibbsite (Norrish & Taylor, 1961; Kämpf & Schwertmann, 1982). Oxalate removes magnetite (Blesa et al., 1986) and, if the reaction is carried out in darkness, it selectively attacks poorer crystallized oxides as well (Mckeague et al., 1966; Schwertmann, 1973). The mixture citrate - bicarbonate - dithionite (CBD) also removes crystalline iron oxides (Mehra & Jackson, 1960) and extracts preferentially pedogenic maghemite over lithogenic magnetite (Singer et al., 1995).

The purposes of this work were (a) to characterize the magnetite of a steatite; (b) to identify its alteration products during pedogenesis, and (c) to put in evidence the usefulness of chemical dissolution methods during sample preparation in order to improve the mineralogical analysis.

MATERIAL AND METHODS

Samples of steatite ("soapstone") and from the B horizon of its overlying CAMBISSOLO (according to the Brazilian Soil Classification System; see EMBRAPA, 1999) were collected at the depth of

40-50 cm, from a soil pedon in Congonhas (20° 29' 59" S 43° 51' 28" W), in the Quadrilátero Ferrífero, a Precambrian geodomain that provides economically exploitable iron ore deposits, in Minas Gerais, Brazil. Cobbles of steatite, some of them presenting easily visible altered zones on the surface of the sample, were collected from an outcropping rock block, in the immediate surroundings of the sampling soil profile.

The soil samples were first broken up by hand, left to dry in air and sieved to obtain the fine earth (mean diameter of particles, $\phi < 2$ mm, saturation magnetization, $\sigma_s = 1.9 \text{ J T}^{-1} \text{ kg}^{-1}$). This fraction was then dispersed with 500 mL $\text{NH}_4\text{OH} \sim 0.6 \text{ mol L}^{-1}$, under stirring in a mixer. The suspension was then sieved, to separate the sand fraction ($\phi = 0.05 - 2$ mm; 17% of the soil mass, $\sigma_s = 4.1 \text{ J T}^{-1} \text{ kg}^{-1}$). The silt ($\phi = 0.002 - 0.05$ mm; 15%, $\sigma_s = 1.0 \text{ J T}^{-1} \text{ kg}^{-1}$) and the clay ($\phi < 2 \mu\text{m}$; 68%, $\sigma_s = 0.31 \text{ J T}^{-1} \text{ kg}^{-1}$) fractions were separated by centrifuging the remainder, according to Jackson (1969). The altered rock material ($\sigma_s = 2.6 \text{ J T}^{-1} \text{ kg}^{-1}$) was separated from about 3-4 cm nearly circular brownish zones clearly identified throughout the cut surface of the greenish matrix of cobbles of rock samples ($\sigma_s = 1.5 \text{ J T}^{-1} \text{ kg}^{-1}$). This altered rock material was sieved to 400 mesh.

The magnetic separates from the ground fresh and the $\phi < 400$ mesh fraction of the altered rock samples and from soil-sand and -silt were obtained from a dilute slurry in water while stirring in a magnetic rod stirrer. The magnetic particles were then separated with a small hand magnet. Except for the fresh rock, a first set of all magnetic extracts were submitted to seven successive treatments with CBD (samples labeled 7xCBD); a second one was independently treated with oxalic acid (28.3 g L^{-1}) + ammonium oxalate (25.2 g L^{-1}) for four hours, with stirring. The four magnetically-extracted (fresh and altered rock and soil sand and silt) and three CBD-treated (all previous ones but the fresh rock) samples were analyzed by XRD with a Rigaku Geigerflex with a graphite diffracted beam monochromator using $\text{Cu}(\text{K}\alpha)$ radiation. NaCl was used as internal standard. Mössbauer spectra were collected at room temperature, and at 160 K under an externally applied magnetic field of 6 tesla, parallel to γ -radiation, in a constant acceleration transmission set up and a $^{57}\text{Co}/\text{Rh}$ source. Saturation magnetization measurements were made with a portable soil magnetometer conceived by Coey et al. (1992). The chemical analysis of the magnetic fractions was carried out by dissolving the sample in hydrochloric acid 1:1. The solution so obtained was then analyzed for iron by the standard dichromatometric method (Jeffery & Hutchison, 1981), and with an Analytical Instruments plasma emission spectrophotometer (mod. Spectroflame) for the other elements. The chemical compositions of the fresh rock, altered rock 7xCBD, sand 7xCBD and silt 7xCBD are presented in Table 1.

Table 1. Chemical composition of magnetic fractions of fresh and altered rocks, sand 7xCBD and silt 7Xcbd

Element	Rock		Soil	
	Fresh	Altered	Sand	Silt
	dag kg ⁻¹			
Fe ₂ O ₃	98.3	93.5	99.8	92.0
Cr ₂ O ₃	1.90	1.66	1.37	1.40
Al ₂ O ₃	0.11	0.67	0.44	0.63
TiO ₂	0.18	0.77	0.09	0.05
MgO	0.80	0.74	0.10	0.06
CaO	0.32	0.35	0.04	0.05
MnO	0.01	0.07	0.06	0.05
LOI ⁽¹⁾	2.0	2.1	1.8	3.0
Total	103.6	99.9	103.7	97.2

⁽¹⁾ Loss on ignition.

RESULTS AND DISCUSSION

The XRD patterns (Figure 1) of the magnetic extracts from the fresh and altered rock (Figure 1a and b) and sand and silt (Figure 1c and d) samples revealed the existence of intense reflections due to an iron-rich spinel phase in all samples, whereas hematite is present in all but the fresh rock samples. As expected, patterns (not shown) for the samples 7xCBD-treated indicate no reflection due to hematite. Residual talc is clearly detected only in the sand and silt samples (Figures 1cd). The lattice

parameter of magnetite ($a = 0.8407(5)$ nm) from the fresh rock (Table 2) is very close to the reported value for pure magnetite ($a = 0.83967$ nm, JCPDS, 1980, card # 19-629). On the other hand, a decrease in the cell dimension can be observed on going from the fresh rock to altered rock, and from soil-sand to -silt. Oxidation of magnetite leads to a smaller unit cell. CBD treatment does not modify significantly the unit cell dimension of magnetite, relatively to the untreated magnetic extract (Table 2), whereas the oxalate-treated samples show an increase of this parameter, that approaches the a -value of the magnetite from the fresh steatite. This result suggests that oxalate preferentially attacks partially oxidized magnetite, which probably coats a more preserved core of the spinel grain. Lattice parameters of the hexagonal cell of the hematite were found to be $a = 0.5036(3)$ nm and $c = 1.375(4)$ nm, determined from the oxalate-treated silt, but similar values were found for this phase from sand and altered rock samples.

Magnetization (σ) values, also given in table 2, indicate that the procedure to remove non-magnetic minerals concentrates the magnetic extract as much as 59-fold for the fresh rock, 28-fold for the altered rock; 16-fold for the sand and 44-fold for the silt samples. The value of $\sigma_s = 88.4 \text{ J T}^{-1} \text{ kg}^{-1}$ for the magnetic extract of the fresh rock in table 2 is well above the characteristic magnetization of pure maghemite $\sigma_s = \sim 60 \text{ J T}^{-1} \text{ kg}^{-1}$ (Coey, 1988). This result, together with the cell parameter given in table 2, confirms that magnetite ($\sigma_s = 100 \text{ J T}^{-1} \text{ kg}^{-1}$, for the pure oxide) is the dominant spinel phase in steatite. Finally, it is seen that σ decreases from the fresh rock to the soil-silt, especially for the untreated samples.

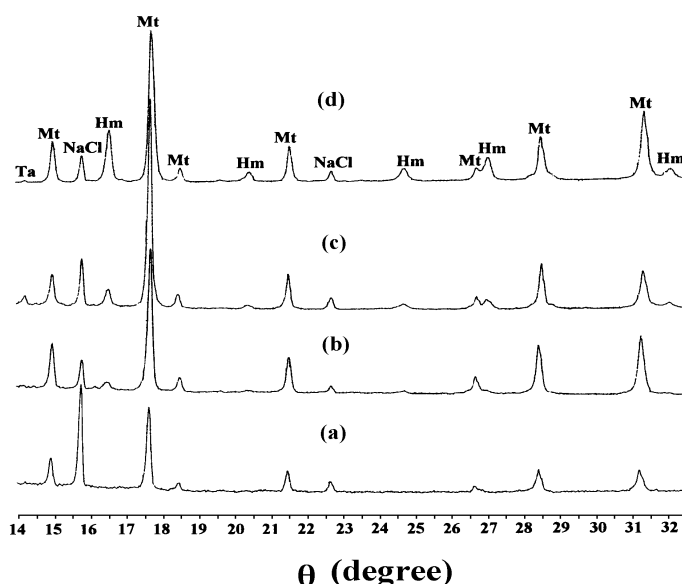


Figure 1. Powder X-ray patterns of (a) fresh rock; (b) altered rock; (c) soil-sand and (d) soil-silt. Radiation CuK α . Hm = hematite, Mt = magnetite, Ta = talc. NaCl = internal standard.

Table 2. Magnetization and unit cell dimension of magnetite of whole magnetic extract and 7xCBD and oxalate-treated rock samples and soil fractions. Typical uncertainties over the magnetization is ~3%

Sample	Magnetization		Unit cell dimension		
	Magnetic extract (ME)	ME treated 7xCBD	Magnetic extract (ME)	ME treated 7xCBD	ME treated Oxalate
	$\sigma/J T^{-1} kg^{-1}$		a_c/nm		
Fresh rock	88.4	nd	0.8407(5)	nd	nd
Altered rock	73.5	75.9	0.8384(6)	0.8384(7)	0.8393(6)
Soil-sand	65.0	77.4	0.8389(3)	0.8395(6)	0.8399(7)
Soil-silt	43.6	71.3	0.8388(6)	0.8385(7)	0.8393(8)

nd: Not determined.

The proportion of hematite as given by Mössbauer analysis in the magnetic extract (Table 3 and Figure 2) increases in the sequence fresh rock (hematite-free) < altered rock < soil-sand < soil-silt. The room temperature hyperfine field of hematite varies from 51.4 T (altered rock) to 51.1 T (soil-silt), which are close to the value of the bulky stoichiometric hematite, 51.8 T (Fysh & Clark, 1982; Murad & Schwertmann, 1986). Spectra of the altered rock and soil-sand and -silt samples show additionally a small central doublet (2-4% of the whole spectral area) which may be assigned to a superparamagnetic hematite (α -Fe₂O₃) together with some ilmenite (FeTiO₃). The absence of any maghemite strongly suggests that, differently from what was reportedly found for the mafic lithology, magnetite is being transformed directly into hematite, in this steatite system. This same conclusion was recently drawn by Lagoeiro (1998) on the magnetite - hematite transformation in Itabira Iron Formation (itabirite) of the same broad geological area of Quadrilátero Ferrífero.

Mössbauer spectra of the 7xCBD treated samples are shown in figure 3, and related fitted parameters are presented in table 4. It can be noted that the outermost sextet due to hematite (quadrupole shift, $\varepsilon \approx -0.2$ mm s⁻¹) of figure 2b through 2d (untreated samples) virtually disappears in figure 3b through 3d (corresponding CBD treated samples), confirming the effectiveness of this selective chemical attack in preferentially removing hematite. Any eventually existing maghemite would be easily detected, particularly in the untreated samples, as its hyperfine field is lower than that of hematite and $\varepsilon \approx 0$. The persisting low intensity (< 4% of the spectral area) doublets may be due to ilmenite. The hyperfine parameters of ilmenite, obtained with low velocity range in full scale (spectrum not shown), were fixed during fitting of magnetic spectra (Tables 3 and 4). Differently from ilmenite of mafic origin (Goulart et al., 1994; Doriguetto et al., 1998), no Fe³⁺ was detected in this case.

Taking into account that the recoilless fraction of the octahedral site $f_{[B]}$ of the spinel structure is 6% lower than that of tetrahedral site $f_{[A]}$ at room temperature (Sawatzky et al., 1969), the ratio Fe^{2+/3+}/Fe³⁺ is 1.98 for the fresh rock, which is virtually the expected value for the stoichiometric magnetite (Fe^{2+/3+}/Fe³⁺ = 2). The hyperfine parameter for all samples (Table 4) is characteristic of pure magnetite.

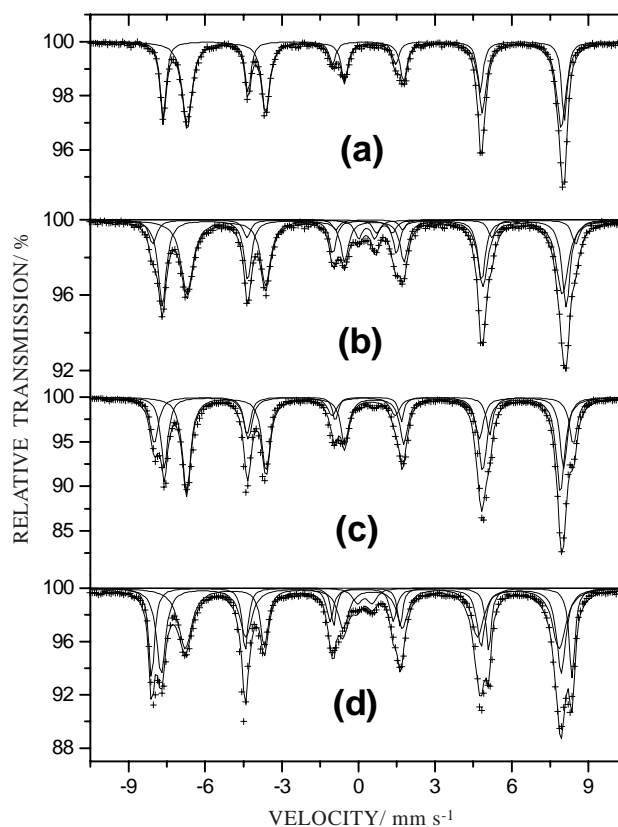


Figure 2. Room temperature Mössbauer spectra of untreated magnetic extracts from (a) fresh rock; (b) altered rock; (c) soil-sand and (d) soil-silt.

Table 3. Room temperature Mössbauer parameters of the whole untreated fractions

Fraction	Silte	Mössbauer parameters			
		B_{hf} /tesla	$(\delta/Fe)/mm\ s^{-1}$	$\epsilon, \Delta/mm\ s^{-1}$	RA
Fresh rock	[Fe ³⁺]	48.7	0.22	-0.017	35
	{Fe ^{3+/2+} }	45.4	0.62	0.004	65
Altered rock	[Fe ³⁺]	49.0	0.23	-0.018	36
	{Fe ^{3+/2+} }	45.6	0.63	0.015	48
	Hm	51.4	0.33	-0.20 ^(*)	10
	I		1.01	0.68	4
	D		0.34	0.58	2
Soil-sand	[Fe ³⁺]	48.5	0.21	0.01	28
	{Fe ^{3+/2+} }	45.4	0.60	-0.03	50
	Hm	50.9	0.30	-0.18 ^(*)	22
Soil-silt	[Fe ³⁺]	48.7	0.23	-0.023	35
	{Fe ^{3+/2+} }	45.5	0.66	-0.020	38
	Hm	51.1	0.32	-0.20 ^(*)	24
	I		1.01	0.68 ^(*)	<1
	D		0.34	0.58 ^(*)	3

B_{hf} = hyperfine field; δ/Fe = isomer shift relative to the metallic iron; ϵ = quadruple shift; Δ = quadruple splitting; RA = relative area of the subspectrum; sites [] and { } refer, respectively, to tetrahedral and octahedral iron sites in the spinel structure; Hm = hematite; I = ilmenite, D = doublet.

(*) Fixed during fitting convergence.

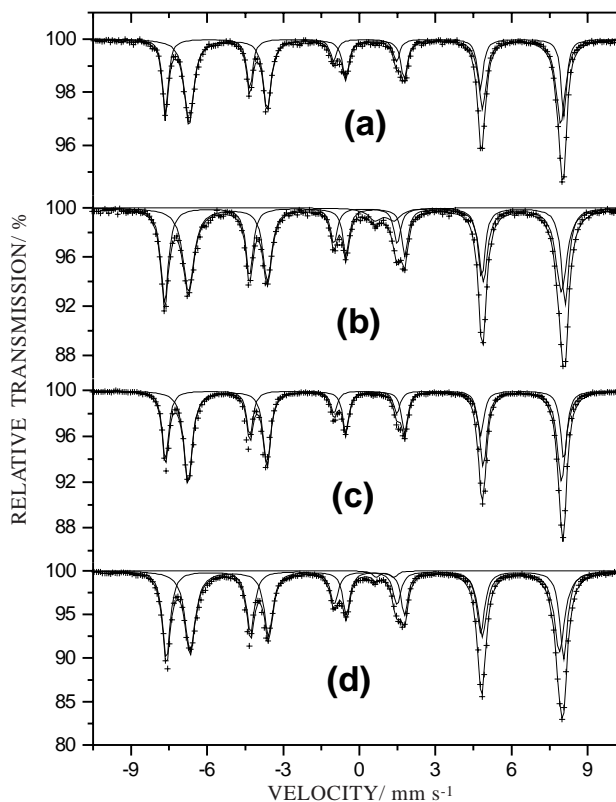


Figure 3. Room temperature Mössbauer spectra from (a) untreated magnetic extract of the fresh rock and treated 7x CBD magnetic extracts from (b) altered rock; (c) soil-sand and (d) soil-silt samples.

Table 4. Room temperature Mössbauer parameters of the 7x CBD treated samples

Fraction	Silte	Mössbauer parameters				
		B_{hf} /tesla	$(\delta/Fe)/mm\ s^{-1}$	$\epsilon, \Delta/mm\ s^{-1}$	RA	$RA_{\{Fe^{3+/2+\}}}/RA_{[Fe^{3+}]}$
Fresh rock	[Fe ³⁺]	48.7	0.22	-0.017	35	1.86
	{Fe ^{3+/2+} }	45.4	0.62	0.004	65	
Altered rock	[Fe ³⁺]	49.0	0.23	-0.023	42	1.29
	{Fe ^{3+/2+} }	45.6	0.62	0.014	54	
	Im		1.02 ^(*)	0.66 ^(*)	4	
Soil-Sand	[Fe ³⁺]	48.7	0.22	-0.025	36	1.78
	{Fe ^{3+/2+} }	45.6	0.61	-0.012	64	
Soil-Silt	[Fe ³⁺]	48.6	0.24	-0.023	45	1.20
	{Fe ^{3+/2+} }	45.2	0.62	-0.020	54	
	Im		1.02 ^(*)	0.66 ^(*)	1	

B_{hf} = hyperfine field; δ/Fe = isomer shift relative to the metallic iron; ϵ = quadruple shift; Δ = quadruple splitting; RA = relative area of the subspectrum; sites [] and { } refer, respectively, to the tetrahedral and octahedral iron sites in the spinel structure; Hm = hematite; I = ilmenite, D = doublet.

(*) Fixed during fitting convergence.

The 6-tesla Mössbauer spectra of CBD-treated samples, obtained at 160 K, are presented in figure 4 and related parameters in table 5. It is interesting to observe that a relatively low-intensity magnetic subspectrum appears in the altered rock and soil-silt samples, which is assigned to uncoupled Fe³⁺ in octahedral spinel sites. In the pair localized hopping model, this pattern corresponds to ferric ion in excess of the number of Fe²⁺-Fe³⁺ pairs in the octahedral site (Coe et al., 1971). No ilmenite is clearly detected in these spectra. Subspectra due to Fe²⁺ and Fe³⁺ in octahedral and Fe³⁺ in tetrahedral sites can now be clearly separated. Some hematite (~7% of the relative subspectral area) also appears in the soil-silt sample. This result reflects the ineffectiveness of CBD attack in removing hematite from the silt sample. Even discarding any eventual difference between *f*-values of octahedral and tetrahedral sites of magnetite, at this temperature, the relative ferrous iron content may be directly derived from in-field Mössbauer data. From the chemical data (Table 1), neglecting other elements smaller than chromium, the following formula is deduced for the fresh rock magnetite, provided that all chromium occupies the octahedral site:



Table 6 presents the spinel formulae for the complete set of samples and the degree of non-stoichiometry (*z*), defined as being the relation given by the spinel formula index (*x*_{Fe}) ratio:

$$x_{[\text{Fe}^{3+/2+}]} / x_{[\text{Fe}^{3+}]} = 2x_{[\text{Fe}^{2+}]} / x_{[\text{Fe}^{3+}]} = 2 - 2z$$

Increases of *z*-values from the fresh to the altered rock and from the soil-sand to -silt fractions reflect the weathering stage of magnetite in this system.

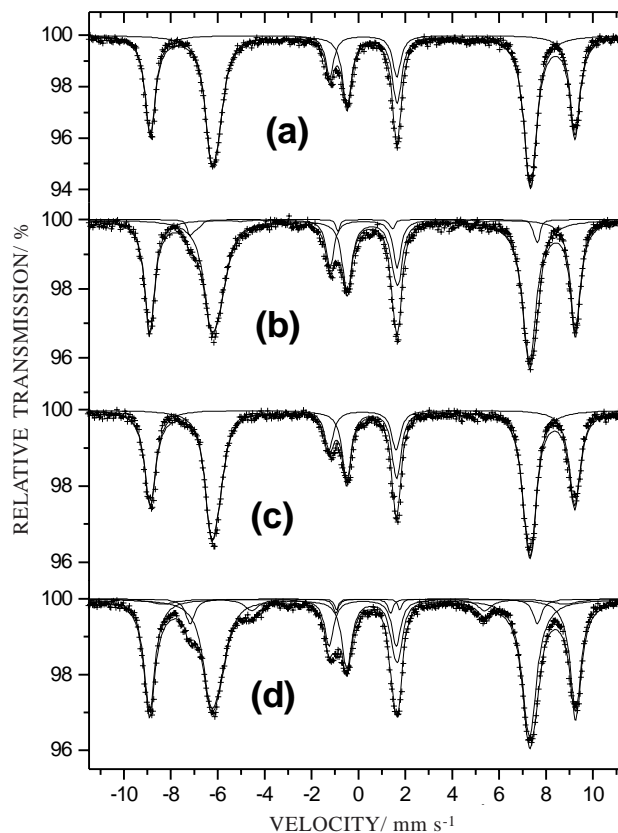


Figure 4. 160 K Mössbauer spectra obtained with an externally applied magnetic field of 6 tesla. (a) Untreated magnetic extract of the fresh rock and treated 7x CBD magnetic extracts from (b) altered rock; (c) soil-sand and (d) soil-silt samples.

Table 5. 160 K in-field (6 tesla) Mössbauer parameters of the 7x CBD treated samples

Fraction	Site	Mössbauer parameters					
		B _{eff} /tesla	B _{hf} /tesla	(δ /Fe)/mm s ⁻¹	ϵ /mm s ⁻¹	RA	RA _{(Fe^{3+/2+})/RA_[Fe³⁺]}
Fresh rock	[Fe ³⁺]	56.2	50.2	0.30	-0.027	35	1.86
	{Fe ^{3+/2+} }	41.9	47.9	0.69	0.018	65	
Altered rock	[Fe ³⁺]	56.3	50.3	0.31	-0.041	35	1.74
	{Fe ^{3+/2+} }	41.7	47.7	0.69	0.042	61	
	{Fe ³⁺ }	45.4	51.4	0.39	0.023	4	
Soil-Sand	[Fe ³⁺]	56.2	50.2	0.28	0 ⁽¹⁾	36	1.78
	{Fe ^{3+/2+} }	41.8	47.8	0.67	0.015	64	
Soil-Silt	[Fe ³⁺]	56.4	50.4	0.29	-0.09	34	1.56
	{Fe ^{3+/2+} }	41.8	47.8	0.68	0.042	53	
	{Fe ³⁺ }	45.9	51.9	0.33	0.023	6	
	Hm	53.2		0.44	-0.18	7	

B_{hf} = hyperfine field; δ /Fe = isomer shift relative to the metallic iron; ϵ = quadruple shift; Δ = quadruple splitting; RA = relative area of the subspectrum; sites [] and { } refer, respectively, to the tetrahedral and octahedral iron sites in the spinel structure; Hm = hematite; I = ilmenite, D = doublet.

⁽¹⁾ Fixed during fitting convergence.

Table 6. Spinel formulae, their corresponding molar masses and degrees of non-stoichiometry (z)

Fraction	Formula ⁽¹⁾	Molar Mass/g mol ⁻¹	z
Fresh Rock	[Fe ³⁺]{Fe ²⁺ _{0.95} Fe ³⁺ _{0.95} Fe ³⁺ _{0.02} Cr ³⁺ _{0.06} }O ₄	230.4	0.05
Altered Rock	[Fe ³⁺]{Fe ²⁺ _{0.89} Fe ³⁺ _{0.89} Fe ³⁺ _{0.13} Cr ³⁺ _{0.05} }O ₄	229.2	0.11
Soil-sand	[Fe ³⁺]{Fe ²⁺ _{0.94} Fe ³⁺ _{0.94} Fe ³⁺ _{0.06} Cr ³⁺ _{0.04} }O ₄	230.3	0.06
Soil-silt	[Fe ³⁺]{Fe ²⁺ _{0.76} Fe ³⁺ _{0.76} Fe ³⁺ _{0.35} Cr ³⁺ _{0.05} }O ₄	226.9	0.24

⁽¹⁾ Cation vacancy.

CONCLUSIONS

1. Magnetite is the iron-rich spinel phase occurring in the fresh and altered rock and in the soil-sand and -silt fractions. The in-field Mössbauer spectrum revealed that a small proportion of Fe³⁺ is not involved in the fast charge transfer in the octahedral site in partially-oxidized magnetite of altered rock and soil-silt fraction.

2. Hematite is detected as an associated mineral in the altered rock and in the sand and silt soil fractions.

3. Nearly stoichiometric and well crystallized magnetite is transformed into hematite during pedogenesis, through progressive oxidation of structural Fe²⁺ to Fe³⁺, in a mineralogenesis pathway markedly different from that observed in mafic systems, where the transformation of the highly substituted magnetite into hematite occurs via maghemite formation.

4. Structural formulae of magnetite with different degrees of non-stoichiometry are proposed, based on relative site populations of the spinel, as given by in-field Mössbauer data.

ACKNOWLEDGMENTS

To Drs. Eddy De Grave (Department of Subatomic and Radiation Physics, Laboratory of Magnetism, University of Gent, Belgium) and Geraldo Magela da Costa (Universidade Federal de Ouro Preto, Brazil) for the Mössbauer measurements with applied magnetic field. To Professor John Michael David Coey (Trinity College Dublin, Ireland) for his helpful discussion and constructive suggestions. Work financially supported by CNPq, FINEP and FAPEMIG (Brazil).

LITERATURE CITED

ALLAN, J.E.M.; COEY, J.M.D.; SANDERS, I.S.; SCHWERTMANN, U.; FRIEDRICH, G. & WIECHOWSKI, A. An occurrence of a fully-oxidized natural titanomaghemite in basalt. *Mineral. Mag.*, 53:299-304, 1989.

BIGHAM, J.M.; GOLDEN, D.C.; BOWEN, L.H.; BUOL, S.W. & WEED, S.B. Iron oxide mineralogy of well-drained ultisols and oxisols: I. Characterization of iron oxides in soil clays by Mössbauer spectroscopy, X-ray diffractometry and selected chemical techniques. *Soil Sci. Soc. Am. J.*, 42:816-830, 1978.

BLESA, M.A.; MARINOVICH, H.A.; BAUMGARTNER, E.C. & MAROTO, A.J.G. Mechanisms of dissolution of magnetite by oxalic acid-ferrous ion solutions. *Inorg. Chem.*, 26:3713-3717, 1986.

COEY, J.M.D.; MORISH, A.H. & SAWATZKY, G.A. A Mössbauer study of conduction in magnetite. *J. Phys.*, C1:271-273, 1971.

COEY, J.M.D. Magnetic properties of iron in soil oxides and clay minerals. In: STUCKI, J.W.; GOODMAN, B.A. & SCHWERTMAN, U., eds. *Iron in soils and clays Minerals*, Dordrecht, Reidel Publishing Company, 1988. p.397-466.

COEY, J.M.D.; GUGAT, O.; MCCAULEY, J. & FABRIS, J.D. A portable soil magnetometer. *R. Fis. Ap. Instr.*, 7:25-30, 1992.

COMISSÃO DE SOLOS DO ESTADO DE SÃO PAULO – CESP. Levantamento de reconhecimento dos solos do Estado de São Paulo. Rio de Janeiro, Serviço Nacional de Pesquisa Agropecuária 1960. (Boletim Técnico, 12)

CURI, N. Lithosequence and toposequence of Oxisols from Goiás and Minas Gerais, Brazil. West Lafayette, Purdue University, 1983 (Tese de Doutorado)

CURI, N. & FRANZMEIER, D.P. Effect of parent rocks on chemical and mineralogical properties of some Oxisols in Brazil. *Soil Sci. Soc. Am. J.*, 51:153-158, 1987.

DEMATTÊ, J.L.I. & MARCONI, A. Effects of drainage on the mineralogy of soils developed from diabase in Piracicaba, State of São Paulo, Brazil. *R. Bras. Ci. Solo*, 15:1-8, 1991.

DORIGUETTO, A.C.; GOULART, A.T.; JESUS FILHO, M.F.; FABRIS, J.D. & SANTANA, G.P. Ilmenite of a soil system developing on amphibolite. *Europ. J. Soil Sci.*, 49:541-546, 1998.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA - EMBRAPA Centro Nacional de Pesquisa de Solos (Rio de Janeiro, RJ). Sistema Brasileiro de Classificação de Solos, Brasília, Embrapa Produção de informação, Rio de Janeiro, Embrapa Solos, 1999. 412p.

FABRIS, J.D.; COEY, J.M.D.; QI, Q. & MUSSEL, W.N. Characterization of Mg-rich maghemite from tuffite, *Am. Mineral.*, 80:664-669, 1995.

- FABRIS, J.D.; JESUS FILHO, M.F.; COEY, J.M.D.; MUSSEL, W.N. & GOULART, A.T. Iron-rich spinels from Brazilian soils. *Hyperfine Interac.*, 110:23-32, 1997a.
- FABRIS, J.D.; MUSSEL, W.N.; COEY, J.M.D.; JESUS FILHO, M.F. & GOULART, A.T. Mg-rich iron oxide spinels from Tuffite. *Hyperfine Interac.*, 110:33-40, 1997b.
- FERREIRA, B.A. Caracterização físico-química de minerais ferruginosos de um pedossistema desenvolvido de basalto. Belo Horizonte, Universidade Federal de Minas Gerais, 1995. p.90 (Tese de Mestrado)
- FONTES, M.P.F.; OLIVEIRA, T.S.; COSTA, L.M. & CAMPOS, A.A.G. Magnetic separation and evaluation of magnetization of Brazilian soils from different parent materials. *Geoderma*, 96:81-99, 2000.
- FYSH, S.A. & CLARK P.E. Aluminous hematite: a Mössbauer study. *Phys. Chem. Miner.*, 8:257-267, 1982.
- GONÇALVES, M.; JESUS FILHO, M.F. & GARG, V.K. Mössbauer study of Brazilian soapstone. *Hyperfine Interac.*, 67:437-442, 1991.
- GOULART, A.T.; JESUS FILHO, M.F.; FABRIS, J.D. & COEY, J.M.D. Characterization of a soil ilmenite developed from basalt. *Hyperfine Interac.*, 91:771-775 1994.
- GOULART, A.T.; FABRIS, J.D.; JESUS FILHO, M.F., COSTA, G.M. & DE GRAVE, E. Iron oxides in a soil developed from basalt. *Clays Clay Miner.*, 46:369-378, 1998.
- JACKSON, M.L. Soil chemical analysis: advanced course. 3.ed. Madison, 1969. p.894.
- JCPDS - Joint Committee on Powder Diffraction Standards, International Center for Diffraction Data, Mineral Powder Diffraction Files Data Book. Swarthmore, Pensilvania, 1980. 1168p.
- JEFFERY, P.G. & HUTCHISON, D. Chemical methods of rock analysis, 3.ed. Oxford, Pergamon Press Oxford, 1981. 379p.
- JESUS FILHO, M.F.; FABRIS, J.D.; GOULART, A.T.; COEY, J.M.D.; FERREIRA, B.A. & PINTO, M.C.F. Ilmenite and magnetite of a tholeiitic basalt. *Clays Clay Miner.*, 43:641-642, 1995.
- KÄMPF, N. & SCHWERTMANN, U. Concentration treatment for iron oxides in soils. *Clays Clay Miner.*, 30:401-408, 1982.
- LADEIRA, E.A.; ROESER, H.M.P. & TOBSCHALL, H.J. Petrogenetic evolution of the green rock belt, Rio das Velhas, Quadrilátero Ferrífero, Minas Gerais. SYMPOSIUM ON THE GEOLOGY OF MINAS GERAIS, 2., Belo Horizonte, 1983. Proceedings. Belo Horizonte, 1983. p.149-159.
- LAGOEIRO, L.E. Transformation of magnetite to hematite and its influence on the dissolution of iron oxide minerals. *J. Metam. Geol.*, 16:415-423, 1998.
- McKEAGUE, J.A. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in Podzols and some other soils. *Can. J. Soil Sci.*, 47:95-99, 1966.
- MEHRA, O.P. & JACKSON, M.L. Iron oxide removal from soils and clay by a dithionite-citrate system buffered with sodium bicarbonate. In: SWINEFORD, A., ed. NATIONAL CONFERENCE ON CLAYS AND CLAY MINERALS, 7., Washington, 1958. Proceedings. London, Pergamon Press, 1960. p.317-327.
- MIJOVILOVICH, A.; MORRAS, H.; SARAGOVIC, C.; SANTANA, G.P. & FABRIS, J.D. Magnetic fraction of an Ultisol from Misiones, Argentina. *Hyperfine Interac. (C)*, 3:332-335, 1998.
- MOUKARIKA, A.; O'BRIEN, F. & COEY, J.M.D. Development of magnetic soil from ferroan dolomite. *Geophy. Res. Letters*, 18:2043-2046, 1991.
- MURAD, E. & SCHWERTMANN, U. The influence of Al substitution and crystallinity on the room-temperature Mössbauer spectrum of hematite. *Clays Clay Miner.*, 34:1-6, 1986.
- MUSSEL, W.N.; FABRIS, J.D.; COEY, J.M.D.; SANS, L.M.A. & LELIS, M.F.F. Compositional and structural variability of Mg-rich iron oxide spinels from tuffite. *R. Bras. Ci. Solo*, 23:791-798, 1999.
- NORRISH, K. & TAYLOR, R.M. The isomorphous replacement of iron by aluminium in soil goethites. *J. Soil Sci.*, 12:294-306, 1961.
- PINTO, M.C.F.; JESUS FILHO, M.F.; GOULART, A.T.; FABRIS, J.D. & SANTANA, G.P. Pedogenic stability of magnetite from amphibolite. *Hyperfine Interac. (C)*, 2:61-66, 1997.
- PINTO, M.C.F.; FABRIS, J.D.; GOULART, A.T. & SANTANA, G.P. Pedogenetic instability of magnetite in mafic lithology. *Hyperfine Interac. (C)*, 3:325-327, 1998.
- RAUEN, M.J. Mineralogical identification of a toposequence of soils from basaltic rocks in the state of Paraná, Brazil. West Lafayette, Purdue University, 1980. (MSc Thesis)
- RESENDE, M.; ALLAN, J. & COEY, J.M.D. The magnetic soils of Brazil. *Earth Plan. Sci. Letters*, 78:322-326, 1986.
- RESENDE, M.; SANTANA, D.P.; FRANZMEIER, D.P. & COEY, J.M.D. Magnetic properties of Brazilian Oxisols. In: INTERNATIONAL SOIL CLASSIFICATION WORKSHOP, Rio de Janeiro, 1988. Proceedings. Rio de Janeiro, 1988. p.78-108.
- ROESER, H.; ROESER, U.; MUELLER & TOBSCHALL, H.J. Petrogenesis of steatites from the southeast of Quadrilátero Ferrífero. In: BRAZILIAN MEETING OF GEOLOGY, 31., Camboriú, 1980. Proceedings. Camboriú, 1980. p.2230-2245.
- ROESER, H.; ROESER, U.; SCHULZ-DOBRICK, B. & TOBSCHALL, H.J. Soapstone - a metasomatic rock. In: SYMPOSIUM ON THE GEOLOGY OF MINAS GERAIS, 4., Belo Horizonte, 1987. Proceedings. Belo Horizonte, 1987. p.286-331.
- SANTANA, D.P. Soil formation in a toposequence of Oxisols from Patos de Minas, Minas Gerais, Brazil. West Lafayette, Purdue University, 1984, p.129. (Tese de Doutorado)

- SAWATZKY, G.A.; WOUDE, V.F. & MORRISH, A.H. Recoilless-fraction ratios for Fe⁵⁷ in octahedral and tetrahedral sites of a spinel and a garnet. *Phys. Rev.*, 183:747-757, 1969.
- SCHWERTMANN, U. Use of oxalate for Fe extraction from soils. *Can. J. Soil Sci.*, 53:244-246, 1973.
- SCHWERTMANN, U. & TAYLOR, R.M. Iron oxides. In: *Minerals in soil environments 2*. ed. Madison, Soil Science Society of America, 1989. p.379-438 (Book Series, 1)
- SIDHU, P.S.; GILKES, R.J. & POSNER, A.M. The behavior of Co, Ni, Zn, Cu, Mn and Cr in magnetite during alteration to maghemite and hematite. *Soil Sci. Soc. Am. J.*, 44:135-138, 1980.
- SINGER, M.J.; BOWEN, L.H.; VEROSUB, K.L.; FINE, P. & TENPAS, J. Mössbauer spectroscopic evidence for citrate-bicarbonate-dithionite extraction of maghemite from soils. *Clays Clay Miner.*, 43:1-7, 1995.