Clays and Clay Minerals, Vol. 47, No. 4, 466–473, 1999.

QUANTIFICATION AND CHARACTERIZATION OF MAGHEMITE IN SOILS DERIVED FROM VOLCANIC ROCKS IN SOUTHERN BRAZIL

ANTONIO CARLOS S. DA COSTA,[1] JERRY M. BIGHAM,[2] FRED E. RHOTON,[3] AND SAMUEL J. TRAINA[2]

[1] Departamento de Agronomia, Universidade Estadual de Maringá, Maringá-PR, CEP 87020-900, Brazil
[2] School of Natural Resources, The Ohio State University, Columbus, Ohio 43210, USA
[3] National Sedimentation Laboratory, USDA-ARS, Oxford, Mississippi 38655, USA

Abstract—Many soils developed from volcanic rocks in southern Brazil exhibit spontaneous magnetization caused by the presence of fine-grained maghemite (γ-Fe_2O_3), but few attempts were made to quantify or characterize this important soil component. To that end, clays were separated from freely drained soils derived from acid ($\geq$63% SiO_2), intermediate (54–62% SiO_2), and basic ($\leq$53% SiO_2) igneous rocks produced by the Paraná flood volcanism. The sample set included soils with a wide range of pedogenic development on different landscape positions. The Fe oxide mineralogy of these samples was examined by using a combination of selective dissolution, magnetic susceptibility, and X-ray diffraction (XRD) techniques. Hematite and maghemite were the primary Fe oxides in mature soils (Oxisols, Ultisols, and Alfisols) developed from basic rocks; whereas goethite was dominant in all other soils, especially those formed from acid-intermediate rocks. The association of maghemite with basic rock materials suggests that it was primarily formed by oxidation of lithogenic magnetite. A strong, positive correlation ($R^2 = 0.89$) was obtained between mass specific magnetic susceptibility (χ) of the clay fractions and maghemite contents estimated by XRD. Either method could be used for quantitative analyses, but χ was more sensitive than XRD at low maghemite concentrations (<2 wt. %). The clay-sized maghemites were superparamagnetic with an estimated value for the mass specific magnetic susceptibility (χ_{lf}) value of 91,000 × 10^{-8} m^3 kg^{-1} and frequency dependent variations of 10–15%. The maghemites also had low unit cell constants, which, if attributed entirely to replacement of Fe by Al, would correlate with Al substitutions in the range of 5–16 mole %. Selective dissolution of the soil maghemites was achieved by treatment of Fe oxide concentrates with 1.8 M H_2SO_4 at 75°C for 2 h.

Key Words—Aluminum Substitution, Ferrimagnetic, Maghemite, Magnetic Susceptibility, Magnetite, Selective Dissolution.

INTRODUCTION

Hematite (α-Fe_2O_3) and goethite (α-FeOOH) are abundant in soils developed from volcanic rocks in southern Brazil, and their properties were studied in detail (*e.g.*, Kämpf and Schwertmann, 1983; Schwertmann and Kämpf, 1985; Palmieri, 1986; Resende *et al.*, 1988; Fontes and Weed, 1991; Fontes *et al.*, 1991). Many soils in this region also exhibit spontaneous magnetization caused by ferrimagnetic Fe oxides such as maghemite (γ-Fe_2O_3) and Ti-maghemite; however, relatively little work was dedicated to understand the nature of these minerals.

The origin of maghemite in soils is controversial. Maghemite may form by burning other Fe oxides in the presence of organic matter (Schwertmann and Fechter, 1984; Anand and Gilkes, 1987), by neoformation from soil solution (Fine and Singer, 1989), or by oxidation of magnetite (Mullins, 1977). Maghemites in the magnetic soils of Brazil may be derived by rapid weathering of magnetite or by direct inheritance from the bedrock (Resende *et al.*, 1986; Coey *et al.*, 1991). Other studies also showed correlation between magnetic properties and the type of parent rock (Curi and Franzmeier, 1987; Fontes and Weed, 1991), intensity of weathering (Santana, 1984), and drainage conditions (Curi and Franzmeier, 1984).

Soil magnetization is useful for mapping and classifying Brazilian soils and was strongly correlated with trace elements that are important plant micronutrients (Resende *et al.*, 1988). Ferrimagnetic minerals (magnetite and maghemite) may also be useful tracer materials in the study of soil erosion (*e.g.*, Dearing *et al.*, 1986). Consequently, routine mineralogic methods, especially selective dissolution and conventional X-ray diffraction (XRD) techniques, for detection and quantification of maghemite in Brazilian soils are needed for an improved understanding of their genesis, fertility, and erodibility. In addition, mass specific magnetic susceptibility (χ) may be useful because the required instrumentation is relatively simple, measurements are rapid and non-destructive, and the method is sensitive to ferrimagnetic Fe oxides at concentrations below the level of detection by XRD. This method was applied to studies of pedogenesis, soil erosion-sedimentation, and pollution (*e.g.*, Le Borgné, 1955; Jones and Beavers, 1964; Mullins, 1977; Ozdemir and Banerjee, 1982; Maher, 1986; Beckwith *et al.*, 1990; Singer *et al.*, 1996; de Jong *et al.*, 1998). The objective of the present study is to use χ in combination with selective dissolution and XRD techniques to obtain quantitative data of maghemite in the clay fractions of soils derived from volcanic rocks in southern Brazil.

Table 1. Toposequence location, parent rock, and soil classification.

Profile	Coordinates		Elevation (m)	Parent rock	Classification[1]	No. of samples
	S. lat.	W. long.				
				Ibiporã		
1	23°23′	51°11′	460	Basaltic Andesite	Rhodic Kandiudalf	10
2	23°23′	51°11′	420	Basaltic Andesite	Lithic Hapludoll	2
3	23°23′	51°11′	480	Basaltic Andesite	Typic Argiudoll	4
4	23°23′	51°11′	520	Basaltic Andesite	Lithic Eutrudox	4
				Campo Mourão		
5	24°02′	52°22′	645	Basaltic Andesite	Anionic Acrudox	7
6	24°02′	52°22′	619	Basaltic Andesite	Anionic Acrudox	5
7	24°02′	52°22′	555	Basaltic Andesite	Typic Troporthent	1
				Tamarana		
8	23°45′	50°54′	640	Quartz Latite	Oxic Humitropept	3
9	23°45′	50°54′	650	Quartz Latite	Typic Kandihumult	7
10	23°45′	50°54′	685	Quartz Latite	Typic Kandihumult	6
				Cruzmaltina		
14	23°58′	51°14′	655	Basaltic Andesite	Typic Kandihumult	6
15	23°58′	51°14′	710	Basaltic Andesite	Typic Troporthent	2
16	23°58′	51°14′	678	Basaltic Andesite	Humic Rhodic Hapludox	7
17	23°58′	51°14′	675	Basaltic Andesite	Anionic Acrudox	8
				Faxinal		
18	23°58″	51°14′	755	Rhyodacite	Humic Hapludox	6
19	23°58″	51°14′	740	Rhyodacite	Humic Hapludox	6
20	23°58″	51°14′	735	Rhyodacite	Lithic Troporthent	1
21	23°58″	51°14′	735	Rhyodacite	Lithic Troporthent	1
Total						86

[1] Soil Survey Staff (1992).

MATERIALS AND METHODS

Maghemite distribution was determined on 86 soil samples (A, B, and/or C horizons) collected from five toposequences in the state of Paraná, Brazil (Table 1). The parent rock for three toposequences (Ibiporã, Campo Mourão, and Cruzmaltina) is a basaltic andesite based on the classification system of De La Roche *et al.* (1980). Soils in the remaining toposequences (Tamarana, Faxinal) were derived from the weathering products of acid-intermediate volcanic rocks with >53% SiO_2. For some analyses, additional samples were obtained from the A and B horizons of freely drained, highly weathered soils (Oxisols) at other locations described by Costa (1996). In all cases, the soils examined in this study were developed from extrusive, igneous rocks produced by the Paraná flood volcanism (Bellieni *et al.*, 1986).

Whole-soil properties

Particle-size distribution of the soil samples was determined according to the pipette method (Camargo *et al.*, 1986). Total C content was measured by a dry combustion procedure (Soil Survey Staff, 1972), and soil pH was measured from 1:2.5 soil-water mixtures. Cation exchange capacity (CEC) and exchangeable Al were determined according to the procedures of EMBRAPA (1979).

Sample fractionation and clay mineralogy

The <2-mm soil materials were dispersed with 0.1 M NaOH and fractionated into sand (2–0.05 mm), silt (0.05–0.002 mm), and clay (<2 μm) separates by a combination of wet sieving and gravity sedimentation in water. The sand and silt fractions were dried at (105°C), whereas the clay fractions were flocculated with 1 M NaCl, washed free of excess salt, frozen, and dried in a lyophilizer. Total Fe (Fe_t) contents were measured by atomic absorption spectrophotometry (AAS) following dissolution of the clays using the method of Bernas (1968). Oriented aggregates of Mg- and K-saturated clays (pre-treated with citrate-bicarbonate-dithionite to remove Fe-oxides) were prepared by using the filter transfer method (Moore and Reynolds, 1989). XRD patterns from the dried aggregates were recorded from 2 to 20 °2θ using CuKα radiation from a Philips PW 1316/90 wide-range goniometer fitted with a theta-compensating slit, a 0.2 mm receiving slit, and a diffracted beam monochromator. Data were collected in a step scan mode (0.02 °2θ for 2 s) and transferred to a computer using a Databox (MDI Inc.) interface and software. Kaolinite, halloysite, gibbsite, hydroxy-interlayered vermiculite, and smectite were identified. Quantitative analyses for kaolinite and gibbsite were obtained by thermogravimetric analysis (Karathanasis and Hajek, 1982).

Concentration of iron oxides

Iron oxides in the soil clays were concentrated for chemical and mineralogic analysis by selectively dissolving kaolinite, halloysite, and gibbsite using the boiling 5 M NaOH procedure of Norrish and Taylor (1961) as modified by Kämpf and Schwertmann (1982).

Selective dissolution of iron oxides

Iron oxides in the untreated clay fractions and the 5 M NaOH residues were selectively dissolved with Na-citrate-bicarbonate-dithionite (CBD) (Mehra and Jackson, 1960). Poorly crystallized Fe oxides were removed from separate samples of the untreated clays with 0.2 M acid ammonium oxalate (AAO) (McKeague and Day, 1966). The Fe and Al contents of both the CBD (Fe_d, Al_d) and AAO (Fe_o, Al_o) extracts were then determined by AAS.

Selective removal of maghemite from the 5 M NaOH residues was accomplished by using a modification of the procedure described by Schwertmann and Fechter (1984). Duplicate, 100-mg samples of the 5 M NaOH residues were weighed into 100-mL polypropylene tubes. The residues were washed once with Na-citrate-bicarbonate (75°C, 15 min) and once with distilled water to remove any readily soluble Fe and Al. The samples were then mixed with 20 mL of 1.8 M H_2SO_4 and held at 75 ± 5°C for periods to 7.5 h. The samples were centrifuged, and the extracts were saved in pre-weighed, 25 mL polyethylene bottles for chemical analysis of dissolved Fe and Al. The solid residues were washed twice with distilled water, dried (110°C for 24 h), and saved for XRD and χ analysis. This procedure effectively removed most of the maghemite and further concentrated hematite and/or goethite.

XRD analysis of iron oxides

Powdered residues from the 5 M NaOH and 5 M NaOH + 1.8 M H_2SO_4 dissolution procedures were mixed thoroughly by agate mortar and pestle with 5% silicon for use as an internal standard. Each sample (100–200 mg) was then side-loaded into an aluminum holder using a glass slide to contain the sample. Diffraction patterns were recorded from 15 to 68 °2θ as previously described, but with a counting time of 5 s. Measurements of both peak position and area were obtained using the Grams 386 v. 2 software (Galactic Industries). Corrections for peak positions were made using a polynomial equation developed from the measured and reported peak positions of the internal standard. The unit-cell size, *a*, of maghemite was calculated from the corrected position of the *d*(220) peak, and the Al substitution was estimated from the following (Schwertmann and Fechter, 1984): mol % Al = $[0.8343 - a\ (\text{nm})]/2.22 \times 10^{-4}$.

Quantitative estimates of hematite and goethite in the 5 M NaOH residues were obtained from the areas of the *d*(012) peak (×3.5) of hematite and the *d*(110) peak of goethite (Schwertmann and Latham, 1986). The area of the *d*(220) diffraction peak (×3.5) of maghemite was used also because there was overlap by any other peak. A factor of 3.5 was used for the selected hematite and maghemite peaks because the relative intensities of these diffraction peaks are ~30% of the maximum.

Magnetic susceptibility

Mass specific magnetic susceptibility was determined for samples of the whole soil, sand, silt, clay, and residue (5 M NaOH and 5 M NaOH + 1.8 M H_2SO_4) using a Bartington MS2 Magnetic Susceptibility System coupled with a MS2B sensor. 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 sample, 10 cm^3 size, were weighed, into 20 cm^3 glass scintillation vials. The volumetric magnetic susceptibility (κ) was measured at both low and high-frequency settings, and the low-frequency mass susceptibility (χ_{lf}) was calculated as follows (Dearing, 1994): $\chi_{lf} = (10\ \kappa_{lf}/m)$, 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 the low and high-frequency settings and was expressed as the percentage dual frequency magnetic susceptibility (Dearing, 1994): $\chi_{fd}\% = [(\kappa_{lf} - \kappa_{hf}/\kappa_{lf}] \times 100]$.

RESULTS AND DISCUSSION

General soil and clay mineralogic properties

Soils from the five toposequences are classified according to parent material, degree of weathering, and stage of profile development to reflect major differences in physical, chemical, and mineralogic properties (Tables 2 and 3). The most highly weathered profiles (Oxisols, Ultisols, and Alfisols) developed from basic rocks generally have a clay content exceeding 70%, low CEC, and low to moderate exchangeable Al. The clay fractions were composed primarily of kaolinite, gibbsite, and Fe oxides with small quantities of hydroxy-Al interlayered minerals. The high degree of weathering of these soils is also reflected in low Fe_o/Fe_d and high Fe_d/Fe_t ratios which suggest that Fe originally present in silicate minerals was released to form crystalline Fe oxides (hematite, goethite, and maghemite).

Less mature soils (Inceptisols, Mollisols, and Entisols) occupying erosional (*e.g.*, shoulder) positions on the same landscapes have lower clay content but high-

Table 2. Selected soil physical and chemical properties.

Parent rock[1]	Soil orders[2]		pH H_2O	Exch. Al %	O.C. %	Clay %	CEC cmol kg^{-1}	χ_{lf} 10^{-8} m^3 kg^{-1}
Basic	Ox-Ult-Alf	$\bar{x}$[3]	5.08	28	1.43	74	10.1	5772
		SD	0.49	28	1.10	9	4.9	1626
Basic	Inc-Mol-Ent	$\bar{x}$	5.97	6	2.48	46	35.0	1431
		SD	0.69	15	1.23	11	16.0	1217
Acid	Ox-Ult-Inc-Ent	$\bar{x}$	4.64	44	1.64	57	11.0	1748
		SD	0.34	26	1.28	9	3.9	1431

[1] Basic = basaltic andesite (SiO_2 ≤53%), Acid = quartz latite or rhyodacite (SiO_2 >53%).
[2] Ox = Oxisol, Ult = Ultisol, Alf = Alfisol, Inc = Inceptisol, Moll = Mollisol, Ent = Entisol.
[3] $\bar{x}$ = mean, SD = standard deviation.

er CEC due to significant quantities of smectite and vermiculite in the clay fractions. The Fe_d/Fe_t ratios were correspondingly lower, and greater proportions of the reductant-soluble Fe oxides were also soluble in AAO indicating the presence of poorly crystalline phases such as ferrihydrite and/or complexation of Fe with humic compounds. These trends suggest that poorly crystalline Fe phases form early in the weathering process along with the release of dissolved silica and organic matter (Blume and Schwertmann, 1969; McKeague *et al.*, 1971).

Soils formed from the acid igneous rocks at Faxinal and Tamarana generally are more kaolinitic with lower pH and higher Al saturation than their basic-rock counterparts. Iron oxide contents (Fe_d) were significantly lower due to fewer ferromagnesian minerals in the parent rocks.

Iron oxide minerals in the soil clays

Dissolution of kaolinite and gibbsite in the clay fractions using boiling 5 M NaOH increased the Fe oxide concentration in the residues from four (highly weathered soil materials) to almost ten-fold (less weathered soil materials) and facilitated the detection of hematite, goethite, and maghemite by XRD. The types and relative amounts of Fe oxides within the toposequence clays depended on the parent material and landscape position (weathering). Hematite and maghemite dominated the Fe-oxide mineralogy of highly weathered profiles developed from basic rocks; in some cases, maghemite comprised as much as 40% of the Fe oxide fraction (Table 3). Goethite was less abundant in these soils, and no goethite was detected by XRD in some samples (Costa, 1996).

By contrast, goethite was much more common in clays from the less-mature soils of the basalt toposequences, and it was usually the dominant Fe oxide in soils developed from acid-intermediate rocks. Maghemite was not detected by XRD in the latter soils (Table 3). Others (Rauen, 1980; Curi, 1983; Palmieri, 1986; Fontes and Weed, 1991) also noted maghemite in soil clays from southern Brazil and suggested that its occurrence was related to the degree of soil weathering, parent rock material, soil depth, and/or drainage conditions. No previous attempt, however, was made to quantify its distribution within or between soil profiles.

Soil magnetic susceptibility

Soils developed from basalt are characterized by higher χ_{lf} values than their counterparts (similar age and landscape position) on acid-intermediate rocks. In both cases, however, the highest values of χ_{lf} were obtained from the maturest soils (Oxisols, Ultisols, and

Table 3. Selected clay (<2 μm) mineralogical properties as related to soil order and parent rock.

Parent rock[1]	Soil orders[2]		Kaolinite	Gibbsite	2:1 Min.	Fe_o	Fe_d	Fe_t	Fe_o/Fe_d	Fe_d/Fe_t	$\frac{Mm}{Mm + Ht + Gt}$[3]	$\frac{Gt}{Mm + Ht + Gt}$
						%						
Basic	Ox-Ult-Alf	$\bar{x}$[4]	61	11	7	0.53	14.4	15.3	0.04	0.93	0.25	0.15
		SD	8	8	4	0.16	2.84	2.53	0.02	0.06	0.10	0.14
Basic	Inc-Mol-Ent	$\bar{x}$	63	2	22	0.96	10.08	12.7	0.11	0.79	0.04	0.71
		SD	11	3	15	0.41	2.09	1.53	0.05	0.10	0.06	0.15
Acid	Ox-Ult-Inc-Ent	$\bar{x}$	68	7	14	0.47	6.68	8.62	0.09	0.76	0.02	0.73
		SD	9	7	8	0.26	2.66	2.71	0.07	0.07	0.04	0.16

[1] Basic = basaltic andesite (SiO_2 ≤53%), Acid = quartz latite or rhyodacite (SiO_2 >53%).
[2] Ox = Oxisol, Ult = Ultisol, Alf = Alfisol, Inc = Inceptisol, Moll = Mollisol, Ent = Entisol.
[3] Mm = maghemite, Ht = hematite, Gt = goethite.
[4] $\bar{x}$ = mean, SD = standard deviation.

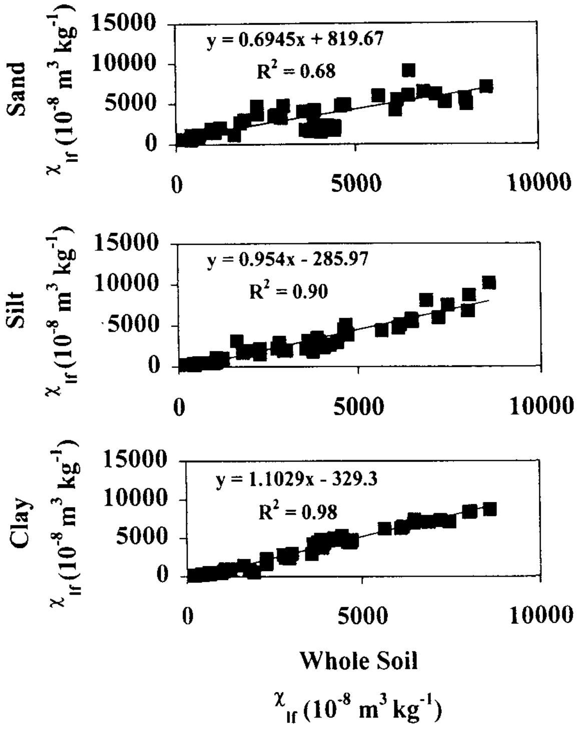

Figure 1. Relationship between mass specific magnetic susceptibilities (χ_{lf}) of sand, silt, and clay fractions and those of the whole soil (<2 mm) materials.

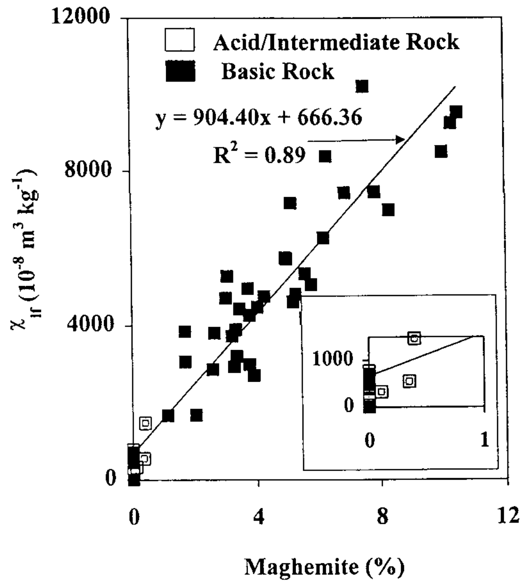

Figure 2. Mass specific magnetic susceptibilities (χ_{lf}) of total clay *vs.* maghemite content determined by XRD. Inset shows data for 0–1% maghemite.

Alfisols) (Table 2). Measurements of χ_{lf} for sand, silt, and clay fractions of the basalt soils showed that all fractions of all horizons (A, B, and C) contained ferrimagnetic components, as expected if these minerals were inherited by weathering of the parent rock (Figure 1). Burning, in contrast, would produce ultrafine maghemite, and only the surface or near-surface horizons would be affected (Mullins, 1977; Dearing, 1994).

Comparisons of χ_{lf} for the whole soil materials and the soil fractions indicate a particularly strong correlation between the clay and whole soil measurements (Figure 1). This relationship is attributed to high clay contents of these soils and to accumulation of clay-sized maghemite during weathering. Measurements of frequency dependent magnetic susceptibility (χ_{fd}) confirmed that superparamagnetic minerals were concentrated in the clay fractions (data not shown). Values of χ_{fd} ranging from 10 to 18% were obtained for the clays as compared to 0–10% for the sand and silt fractions. Lower values of χ_{fd} for the sand and silt fractions indicate a mixture of superparamagnetic maghemite and coarse, single, or multi-domain magnetite (Dearing, 1994). The increase in χ_{fd} with decreasing grain size suggests that comminution of the magnetite-maghemite grains occurred during weathering. Low Fe_o values from the clay fractions indicate that the maghemites are fully oxidized because structural Fe^{2+} catalyzes the dissolution of magnetite-maghemite in AAO (Rhoton *et al.*, 1981).

Quantification of maghemite in soil clays by magnetic susceptibility

Values of χ_{lf} from the soil clays were strongly correlated with maghemite content calculated from the products of CBD-extractable Fe_2O_3 and the proportions of maghemite obtained by XRD analysis of the 5 M NaOH residues (Figure 2). Although the correlation statistic is high ($R^2 = 0.89$), XRD analysis failed to detect maghemite in clays from the least weathered profiles and those soils developed from acid-intermediate rocks. Detection limits were affected because the most intense diffraction peak of maghemite (311) has a similar *d*-value to the second most intense diffraction peak (110) of hematite. Analysis of maghemite in mixed assemblage with hematite and goethite is also difficult using Mössbauer spectroscopy because the minerals yield spectra that superpose in the absence of an external magnetic field (Fontes *et al.*, 1991). By contrast, magnetic susceptibility is a simple and sensitive method for detecting small amounts of fine-grained maghemite in soil clays. Quantitative estimates of maghemite by magnetic susceptibility may also be possible; however, the χ_{lf} of the maghemite must be known because variations may be induced by differences in particle size, shape, and chemical composition (Coey, 1988; Dearing, 1994). Magnetic susceptibility values reported for maghemite (Dearing, 1994) range from 44,000 to 111,600 × 10^{-8} m^3 kg^{-1}. From the data in Figure 2, the χ_{lf} of the soil maghemites in this study is ~91,000 × 10^{-8} m^3 kg^{-1}.

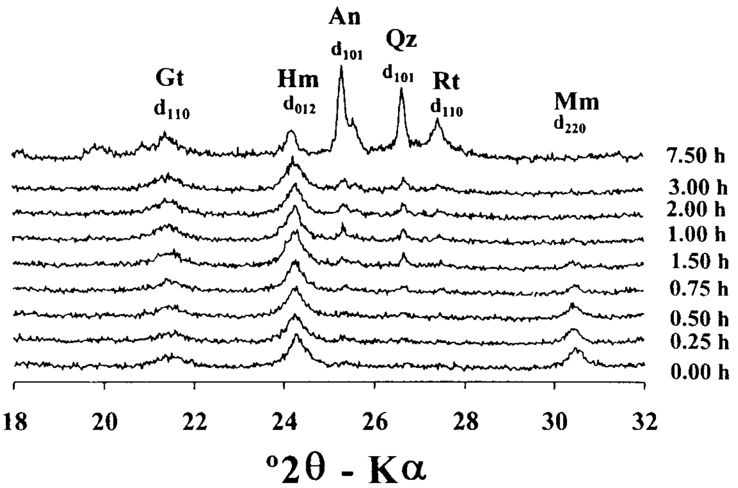

Figure 3. Sequential XRD patterns from a representative 5 M NaOH residue following exposure to 1.8 M H_2SO_4 (75°C) for <7.5 h. Qz = quartz, Gt = goethite, Hm = hematite, An = anatase, Rt = rutile, Mm = maghemite.

Selective dissolution of soil maghemites

Schwertmann and Fechter (1984) found that soil maghemites separated with a hand magnet could be selectively dissolved with 1.8 M H_2SO_4 at 80°C for 7.5 h. In the present study, 5 M NaOH concentrates from Oxisol clays containing maghemite were likewise extracted with 1.8 M H_2SO_4. The dissolution of maghemite was monitored, in selected samples, by observing the intensity of the *d*(220) diffraction peak (Figure 3), and the change in χ_{lf} of the residues with time (Figure 4). Although it is not proven that goethite and hematite were unaffected by the acid treatment, after 7.5 h the diffraction peaks of both minerals increased in intensity whereas the *d*(220) peak of maghemite was unobserved. In addition, the magnetic susceptibilities of the test samples were reduced to <5% of original values over a 2 h period. Changes in the rate of Fe (and Al) released to solution also occurred after 2 h (Figure 5). Maghemite and some associated hematite dissolved after 7.5 h, as shown by relative increases in the XRD peak areas of residual anatase, quartz, and rutile (Figure 3). Based on these results, a reaction time of 2 h is recommended for selective dissolution of maghemites in soil clays.

Al substitution

Magnetic Fe oxides may be widely variable in chemical composition (Anand and Gilkes, 1984), and foreign ions may change the unit-cell volume. Soil maghemites examined in this study all have small unit-cell constants based on the position of the *d*(220) XRD peak. If the decrease is attributed entirely to replacement of Fe by Al, substitutions in the range of 5–16 mol % may be calculated by using the relationship (see above) between a_0 and mol % Al reported by Schwertmann and Fechter (1984). These results are consistent with those obtained by Schwertmann and Fechter

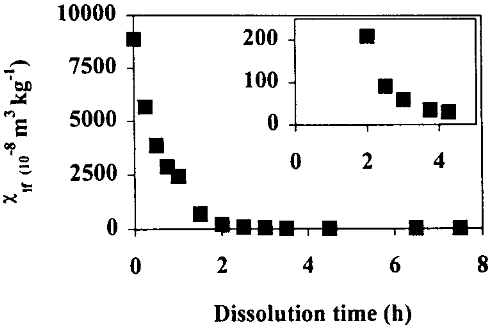

Figure 4. Mass specific magnetic susceptibility (χ_{lf}) of a representative 5 M NaOH residue as a function of dissolution time in 1.8 M H_2SO_4. Inset shows data for 0–4 h period.

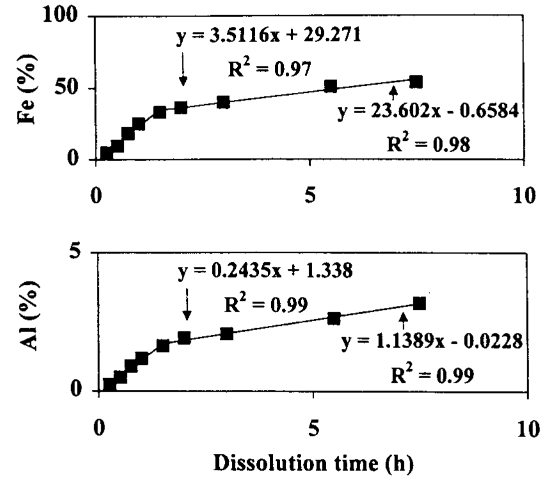

Figure 5. Dissolved Fe and Al in representative 1.8 M H_2SO_4 (75°C) extracts expressed as percentages of the CBD-extractable Fe and Al as a function of dissolution time.

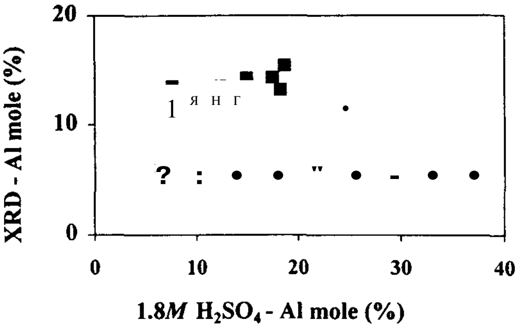

Figure 6. Relationship between Al substitution in maghemite measured by XRD *vs.* extraction with 1.8 M H_2SO_4.

(1984), Wolska and Schwertmann (1989), and Fontes *et al.* (1991).

Al substitutions calculated from the ratio of Fe and Al released to solution after 2 h of contact with H_2SO_4 (Figure 5) showed no correlation with those derived by XRD (Figure 6). Al in the sulfuric-acid extracts generally is higher (<40 mol % Al) than predicted by XRD results, and these values were probably affected by release of Al from residual 2:1 phyllosilicates in the 5 M NaOH concentrates. Additional efforts to better define the extent of metal substitution in maghemite and the resulting effects on mineral chemistry are warranted because this study suggests that maghemite may comprise <50% of the Fe oxides in some soil clays.

ACKNOWLEDGMENTS

A.C.S. da Costa acknowledges the financial support from CAPES (Coordenadoria de Aperfeiçoamento de Pessoal de Nfvel Superior), under process 2631/91-7. We also thank U. Schwertmann of the Tech. Universitat Munchen and an anonymous reviewer for the helpful comments and suggestions on our manuscript.

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(Received 16 October 1997; accepted 17 December 1998; Ms. 97-094)