

## IRON OXIDE-CLAY MINERAL ASSOCIATION IN BRAZILIAN OXISOLS: A MAGNETIC SEPARATION STUDY

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**Abstract**—Selected Brazilian Oxisols were sampled and submitted to high-gradient magnetic separation (HGMS) to study the iron oxide-clay mineral associations. The soils, derived from four different parent materials, have mineralogy dominated mostly by hematite, goethite, and kaolinite. Gibbsite appears in most soil samples. The high-gradient magnetic separation showed good separation for some soils, as indicated by color differentiation and iron oxide segregation between magnetic and nonmagnetic fractions. Soils that showed a somewhat low surface area for the iron oxides associated with high phosphate adsorption were poorly separated by HGMS. This suggests a strong interaction between kaolinite and iron oxides, which would indicate a low estimation of their surface areas obtained by the difference method using BET-N<sub>2</sub> data. A relative concentration of anatase and rutile in the magnetic portion of some of the samples was attributed to the presence of Fe, either as coatings on the crystals or within the structure of these two minerals.

**Key Words**—Brazil, Goethite, Hematite, Magnetic separation, Oxisols.

### INTRODUCTION

In general, Brazilian Oxisols have very good physical characteristics, including high porosity, low bulk density, and a very stable granular structure. This is true even for the clayey Oxisols which may contain 70–80% clay. As they usually have their mineralogy dominated by hematite, goethite, kaolinite and gibbsite, it is believed that the association of the Fe oxides with kaolinite, and sometimes gibbsite, is responsible for such structure where the clay-size particles are so highly aggregated that they behave as sand particles. The association of silicate clays and Fe oxides for stabilizing soil aggregates has yet to be proven. Greenland and Oades (1968) and Greenland (1975) showed that kaolinite-iron oxide complexes formed under alkaline conditions were merely mechanical mixtures, and the kaolinite surface had not become coated by the Fe oxide. However, where Fe oxyhydroxide was precipitated on kaolinite surfaces at pH 3.0, sorption of the positively-charged particles caused reduction of both the specific surface area and the permanent negative charges of the complex. Golden and Dixon (1985) studied the association of kaolinite and several synthetic Fe oxides and concluded that the presence of silicate as an adsorbed anion on kaolinite inhibited Fe oxide crystallization from “ferric hydroxide” gel and facilitated an intimate coulombic association between fine, positively-charged Fe oxide particles and kaolin. On the other hand, phosphate did not affect the crystallization of Fe oxides or the kaolinite-iron oxide association.

Magnetic separations, which take advantage of the magnetic properties of minerals, have had industrial applications for many years. Schulze and Dixon (1979) adapted high-gradient magnetic separation (HGMS) to

the study of soil clays with the main purpose of concentrating Fe oxides. They placed a filter made of fine, stainless steel wool in a strong magnetic field, to provide the strong gradient necessary to trap weakly magnetic clay-size particles from a flowing suspension. Subsequently, HGMS has been successfully used in soil mineralogy to concentrate Fe oxides in different ways for different purposes (Hughes, 1982; Hughes and Le Mare, 1982; Russell *et al.*, 1984; Golden and Dixon, 1985; Ghabru *et al.*, 1988).

The objective of this research was to use high-gradient magnetic separation on selected clay samples from Brazilian Oxisols to evaluate the degree of association between the soil iron oxides and the other clay-size minerals, particularly kaolinite.

### MATERIALS AND METHODS

Soil samples from the B horizons of Oxisols were collected at 1 m depth. The soils are all from the Triângulo Mineiro region and are representative of important Brazilian Oxisols. The main characteristics of these soils are presented in Table 1.

Organic matter was destroyed with sodium hypochlorite (Anderson, 1963) and the total clay fractions (<2 μm) were separated by gravity settling (Jackson, 1979) after clay dispersion. In total clay samples, and/or clays separated by HGMS, the following analyses were performed: (1) color by Munsell Soil Chart on dry samples in diffuse daylight; (2) citrate-dithionite (CD) extraction of Fe oxides (Coffin, 1963); (3) surface area by N<sub>2</sub> gas adsorption; (4) X-ray diffraction using Ni-filtered CuKα radiation and a diffracted-beam monochromator; and (5) phosphate adsorption using the Langmuir equation to estimate adsorption parameters.

Table 1. Soil taxonomy, parent material, and mineralogical composition of the soils.

Sample	Soil taxonomy	Parent material	Mineralogy
S <sub>1</sub>	Typic Acrustox	Cenozoic Clayey Sediments	K, Gb, Gt, H
S <sub>2</sub>	Typic Acrustox	Cenozoic Clayey Sediments	K, Gb, Gt, H
S <sub>3</sub>	Typic Acrustox	Cenozoic Clayey Sediments	Gb, K, Gt, H
S <sub>4</sub>	Typic Acrustox	Sandstone	K, H, Gt
S <sub>5</sub>	Typic Eustrustox	Sandstone	K, H
S <sub>6</sub>	Typic Acrustox	Basalt	K, H, Gb
S <sub>7</sub>	Rhodic Acrustox	Basalt	K, H, Gb
S <sub>8</sub>	Typic Acrustox	Schist	K, Gb, Gt, H

K = kaolinite, Gb = gibbsite, H = hematite and Gt = goethite.

The surface area of the Fe oxides was calculated from the surface-area data of total clay samples and deferrated (CD-treated) samples. The difference method employed is based on the adsorption of the inert gas (N<sub>2</sub>) before and after extracting the iron oxides, and expresses the difference per unit weight of Fe oxide extracted. Aluminum substitution in the Fe oxides was calculated from the Al removed by the citrate-dithionite (CD) extraction.

#### High-gradient magnetic separation

A magnetic filter was prepared and assembled to make up the apparatus essentially as described by Schulze and Dixon (1979). Total clay samples (<2.0 μm) were dispersed using an ultrasonic probe for about 30 s and diluted with water (pH 10) to give a 0.2% suspension. All suspensions were passed through the magnetic filter three times at a flow rate of 120–140 cm<sup>3</sup>/min (flow velocity of 1.50–1.75 × 10<sup>-2</sup> m/s). There was a good color differentiation between the magnetic fractions and the tailings for most samples. For a few of the samples most of the clay was retained in the magnetic filter with just a slightly turbid tailing sus-

pension. Only these samples were passed through the filter again at a faster flow rate (320–340 cm<sup>3</sup>/min; 4.01–4.27 × 10<sup>-2</sup> m/s flow velocity), to improve the concentration. The magnetic field was controlled at 1.0 tesla (1 T).

After the suspension had passed through the filter and was collected, pH-10 water was passed through at the same flow velocity with the magnet on to clean the system. Material collected that was nonmagnetic at 1 T was considered the *nonmagnetic* fraction. Then the magnet was turned off and the magnetically-trapped material, the *magnetic* fraction, was flushed out. All the clays were passed through the filter three times.

The magnetic and nonmagnetic fractions were flocculated by adjusting the suspensions to pH 3.5–4.0. The clear supernatant solution was siphoned off, and the clay material was freeze-dried and stored for subsequent analyses.

## RESULTS AND DISCUSSION

The HGMS technique causes paramagnetic or antiferromagnetic Fe oxides to be attracted to a magnetic filter. Minerals like kaolinite or gibbsite, which are composed mainly of diamagnetic atoms are much less affected. Therefore, the degree of concentration of Fe oxides is expected to be high if the association between Fe oxides and the other components is not very intimate.

Iron extracted by citrate-dithionite (Fe<sub>d</sub>), the proportion of the Fe found in magnetic and nonmagnetic fractions, the color, and the Al substitution determined from CD extraction and surface area are presented in Table 2.

From these data it can be seen that for some samples the concentration of iron oxide was very effective, whereas for others it was not. The samples where the concentration was not very effective are S<sub>6</sub> and S<sub>7</sub>; samples from mafic rocks (basalt). These samples were passed through the magnetic filter at the faster flow velocity in order to achieve some separation. At the slower flow velocity almost all the clay was retained in the filter. The relative proportions of Fe in the magnetic and nonmagnetic fractions are quite similar (Table 2). Figure 1 shows a comparison of the XRD pat-

Table 2. Iron removed by citrate-dithionite, Fe<sub>d</sub>, clay color, Al substitution in citrate-dithionite extract, and surface area by BET-N<sub>2</sub> for the samples separated by high gradient magnetic separation.

Sample	% Fe <sub>d</sub>	% Fe	Munsell color	Al-CD (mol %)	Surface area (m <sup>2</sup> /g)
S <sub>1</sub> MAG	6.70	72	5 YR 5/8	22.4	34
NMAG	2.55	28	7.5 YR 7/8	34.6	39
S <sub>2</sub> MAG	4.67	67	2.5 YR 5/6	17.0	37
NMAG	2.35	33	7.5 YR 7/8	30.1	43
S <sub>3</sub> MAG	21.82	88	2.5 YR 5/8	12.1	42
NMAG	2.97	12	7.5 YR 7/8	29.7	46
S <sub>4</sub> MAG	32.02	80	2.5 YR 3/4	10.3	51
NMAG	7.85	20	2.5 YR 4/8	18.6	83
S <sub>5</sub> MAG	25.27	72	10 R 3/4	4.2	36
NMAG	9.92	28	10 R 4/8	5.2	48
S <sub>6</sub> MAG	23.20	60	2.5 YR 3/6	9.4	48
NMAG	15.6	40	2.5 YR 4/8	10.2	51
S <sub>7</sub> MAG	19.67	60	2.5 YR 3/6	10.5	49
NMAG	12.84	40	2.5 YR 4/8	11.6	50
S <sub>8</sub> MAG	15.19	68	5 YR 5/8	16.7	32
NMAG	7.03	32	5 YR 7/8	21.8	48

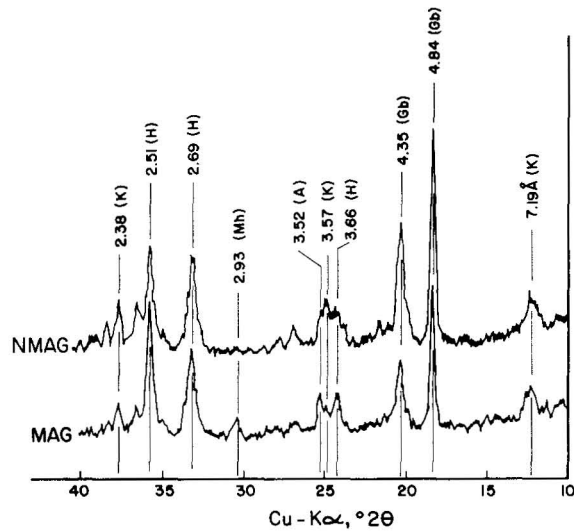


Figure 1. X-ray diffraction patterns of magnetic and non-magnetic fractions of sample  $S_6$  (randomly-oriented sample). K = kaolinite; H = hematite; Mh = maghemite; A = anatase; Gb = gibbsite; Gt = goethite; R = rutile.

terms of the magnetic and nonmagnetic fractions for sample  $S_6$ . The peak intensities for kaolinite are not very different, suggesting that similar amounts of this mineral are present in both fractions. The gibbsite peaks show a decrease in the magnetic fraction and peaks for Fe oxides are very similar.

This result suggests that a kaolinite-Fe oxide or kaolinite-Fe oxide-gibbsite association exists and is what causes the poor separation and concentration of the iron oxides for these samples. Also, there is a good possibility that this association could explain the very high phosphate adsorption (Table 2) correlated with relatively low Fe-oxide surface areas for the soil samples from mafic rocks. The surface area may have been underestimated by the difference method, which does not take into account the common surface area of associated particles, in this case the common surface area of kaolinite and hematite. The data on phosphate adsorption and surface area (Table 3) shows that the surface areas of these samples were among the lowest, while the phosphate adsorption was among the highest. Differential X-ray diffraction from these samples showed very small crystallite size ( $MCD_{110} \approx 35$  nm) for these hematites (Fontes and Weed, 1991). It suggests that the size of these hematite particles probably made the interaction between them and the kaolinite particles easier.

The samples of the soils from sandstone ( $S_4$ ,  $S_5$ ) exhibited good separation of the Fe oxides as indicated by the amounts of Fe extracted and the color differences between the magnetic and nonmagnetic fractions. The flow velocity through the magnet for these suspensions was  $1.50-1.75 \times 10^{-2}$  m/s, a much lower rate than

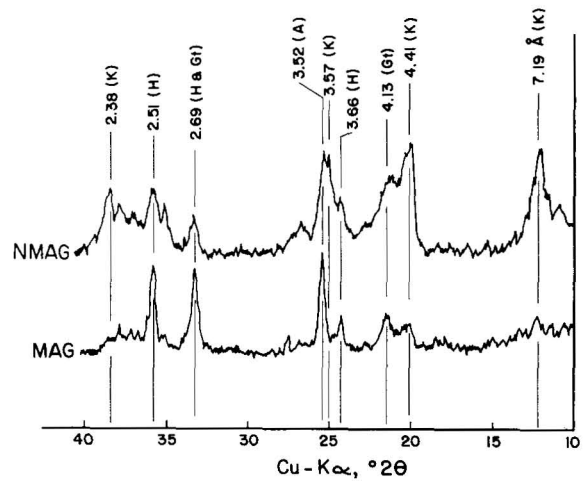


Figure 2. X-ray diffraction patterns of magnetic and non-magnetic fractions of sample  $S_4$  (randomly-oriented sample).

used for the soil samples from mafic rocks. Comparison of the XRD relative intensities in Figure 2 shows that the amount of kaolinite in the magnetic fraction is less than that in the nonmagnetic fraction. This suggests that any kaolinite-Fe oxide association is less intimate than for the mafic samples. Fontes and Weed (1991) found a large crystallite size ( $MCD_{110} \approx 85$  nm) for hematites from sandstone-derived soils. The large size of these hematite particles seems to work against any strong interaction between hematite and kaolinite. A well-defined peak for anatase occurs in the pattern of the magnetic fraction. In the nonmagnetic fraction this peak is partially overlapped by the (002) peak of kaolinite. Anatase is present in both fractions but is relatively concentrated in the magnetic fraction. The peak ratio anatase/kaolinite is 4.43 in the magnetic fraction whereas in the nonmagnetic fraction the ratio is 1.11.

Table 3. Surface areas (BET- $N_2$ ) for total and deferrated samples; calculated surface areas for the Fe oxides; phosphate adsorption maxima for total clay samples calculated using the Langmuir isotherm.

Sample	Total clay	Clay-Fe <sup>1</sup>		Adsorption max.
		m <sup>2</sup> /g		
				μmole P/g
$S_1$	44	38	62	134
$S_2$	42	39	67	125
$S_3$	48	42	85	153
$S_4$	80	77	93	134
$S_5$	44	43	45	69
$S_6$	52	51	54	155
$S_7$	52	51	56	139
$S_8$	43	37	68	133

<sup>1</sup> Surface area of the deferrated clay samples.

<sup>2</sup> Surface area of Fe oxides calculated by the difference method.

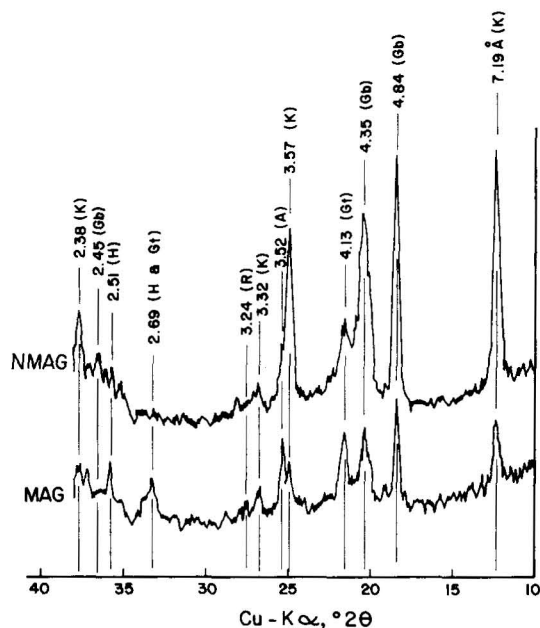


Figure 3. X-ray diffraction patterns of magnetic and non-magnetic fractions of sample  $S_2$  (randomly-oriented sample).

The samples of the soils derived from clayey sediments ( $S_1$ ,  $S_2$ ,  $S_3$ ) show differential concentration. In  $S_2$  the nonmagnetic fraction contains only goethite and the magnetic fraction both hematite and goethite (Figure 3). Again, anatase is clearly evident in the magnetic fraction and rutile is also present.

Sample  $S_3$  showed the best differential concentration among the soils from the clayey sediments because it contains more hematite. The good relative concentration is shown by the amounts of Fe, the Al-substitution data, and by the color difference between the red magnetic fraction and the yellow nonmagnetic fraction. This sample also showed a relative concentration of anatase in the magnetic fraction. The comparison of the anatase/kaolinite peak ratio shows values of 2.30 for the magnetic and 0.62 for the nonmagnetic fractions. Figure 4 shows the X-ray patterns for the magnetic and nonmagnetic fractions of sample  $S_3$ .

The Al substitution in the Fe oxides was calculated from the Al removed by CD extraction. The rationale for using Al-substitution data as calculated by CD extraction is the following: dithionite dissolves Fe oxides preferentially by reduction of  $Fe^{3+}$  to  $Fe^{2+}$ . In doing so it releases Al from the iron-oxide structure. The citrate could dissolve poorly-crystalline phases that contain Al, however, this interference is minimized for two reasons. First, these phases exist in low amounts in the B horizons of such highly-weathered soils, and second, and more important, the long exposure (5–6 hours) of the clay to pH-10 water, together with the use of the ultrasonic probe, would have helped to dis-

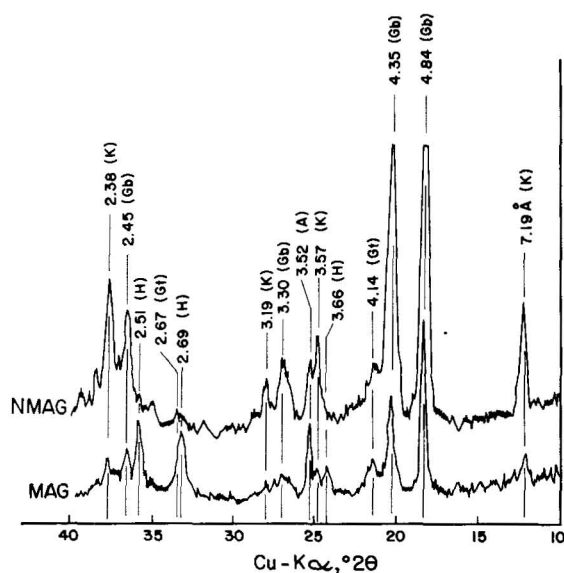


Figure 4. X-ray diffraction patterns of magnetic and non-magnetic fractions of sample  $S_3$  (randomly-oriented sample).

solve poorly crystalline phases prior to the CD treatment. Therefore, the Al measured by the CD treatment may be taken as a good estimate of Al substitution in the Fe-oxide structure of the samples separated by HGMS.

Al-substitution data seem to support the XRD and color data indicating that there is hematite segregation in the magnetic fraction of some samples. In all samples where goethite is present in a reasonable amount, segregation has resulted in higher Al substitution in the Fe oxides of the nonmagnetic fraction. Hematite normally takes up much less Al in its structure than does goethite (Schwertmann, 1988).

Anatase is relatively concentrated in the magnetic fraction of most samples, implying that it is trapped magnetically. Schulze and Dixon (1979) attributed the magnetic trapping of anatase to the positive magnetic susceptibility of titanium oxides (Weast, 1975). However, the magnetic susceptibility of the titanium oxides is too small to explain this magnetic trapping. Therefore, if anatase and rutile ( $TiO_2$ ) are not paramagnetic, their magnetic trapping must be accounted for either by the presence of structural Fe or the presence of Fe oxides intimately associated with them. Iannicelli (1976) used high extraction magnetic filtration (HEMF) to brighten kaolin by removing submicron-size magnetic contaminants. He found a dramatic reduction in  $Fe_2O_3$  and  $TiO_2$  in the samples, and Fe-stained anatase was the principal mineral contaminant extracted. Weed and Bowen (1990), working with HGMS to study hydroxy-interlayered minerals in deferrated samples, reported that iron-substituted Ti oxides, including rutile, ilmenite, anatase, and pseudorutile were found in the fractions separated in low magnetic fields.

## CONCLUSIONS

A very good separation between iron oxides and clay minerals in soils from sandstone suggests that the large crystallite size for the hematite in these soils does not favor strong, intimate interaction with kaolinite.

In the soils from mafic rocks, the small crystallite size of the hematite favors interaction with kaolinite. This interaction resulted in a poor HGMS separation. These samples showed a somewhat low surface area for the iron oxides (calculated by the difference method), even though it was associated with very high phosphate adsorption.

There is some segregation between hematite and goethite, with hematite being preferentially concentrated in the magnetic fractions. This is suggested by the XRD patterns and the color differentiation of some samples, and is further supported by the lower Al substitution in the magnetic fractions as compared to the nonmagnetic fractions.

Ti oxides are concentrated in the magnetic fraction, and were accounted for by either the presence of structural Fe or the presence of intimately-associated Fe oxides.

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