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ABSTRACT

Research was conducted to evaluate Fe transformations in a hydrosequence of Oxisols from the Central Plateau of Brazil. The best-drained member of the hydrosequence of soils selected for the study classifies as an Anionic Acrustox (Dark-Red Latosol) and has codominant hematitic and goethitic iron oxide mineralogy and reddish hues (2.5 YR). X-ray diffraction and chemical extraction techniques were used to make detailed analyses of the iron oxides. Peak positions for hematite are coincident with those reported for hematite without foreign ion substitution. Peak positions for goethite are shifted toward a lower *d*-spacing, which corresponds to 34 mole % of AlOOH substituting for FeOOH. Soil samples from the Bo horizon were subjected to reducing conditions in the laboratory over a range of time periods, using sucrose as a source of energy to speed up the activity of the soil microorganisms. The observed changes in soil mineralogies confirm the preferential reduction and removal of hematite over goethite. Mineralogies and soil colors after reduction treatments are comparable to that of the Anionic Acrustox (Red-Yellow Latosol) found in the wetter section of the hydrosequence. The results of this study support the hypothesis that differences in color and iron oxide mineralogy of soils in this hydrosequence are the result of the preferential reduction of hematite over Al-substituted goethite in the presence of a seasonally high water table.

MOST "BRIGHT COLORED" soils of the Tropics contain iron oxides (considered in this paper as a group name for iron oxides and oxyhydroxides) of varying amount, form and crystallinity according to pedogenic environment (Schwertmann and Taylor, 1977). Hematite and goethite are reported respectively as red and yellow-brown coloring agents for soils (Schwertmann and Taylor, 1977; Bigham et al., 1978). The ratio of hematite to goethite is governed by several factors. Factors of particular importance include: rate of Fe release from primary minerals, organic matter content, pH, soil temperature, and soil moisture (Schwertmann, 1985).

Several field studies have reported iron oxide mineralogies in relation to topographic position. Curi and Franzmeier (1984) examined a toposequence in which reddish soils, having dominantly hematite, occurred in the upper well-drained positions; yellowish soils, having dominantly goethite, were found in the lower landscape positions where the soil environment was more moist. In a toposequence, described by Williams and Coventry (1979), yellowish soils, having dominantly goethite, were found on landscapes where a shallow lithologic contact impeded drainage. Highly permeable soils had dominantly hematite. In both of these studies, the differences in iron oxide mineralogies were attributed to conditioning of the soil environment which affected the mineralogy of Fe that was released and oxidized upon weathering of primary minerals.

In a recent study of the relationship between soil color and water table fluctuation in a hydrosequence of Oxisols in Brazil, Macedo and Bryant (1987) developed an alternative hypothesis that yellowish soils formed as the result of an adjustment of Fe mineralogy from mixed hematitic and goethitic mineralogy to purely goethitic Fe mineralogy in response to a change to a wetter moisture regime brought about by climatic changes and landscape evolution. However, whether both hematite and goethite from the upper part of the soil profile have been dissolved by microbial reduction of Fe(III) to Fe(II) and the Fe(II) subsequently reoxidized as goethite, or whether only hematite has been selectively dissolved by microbial reduction to Fe(II) and subsequently migrated to the lower part of the profile, remained unclear.

The requirements for reduction in soils are the presence of microorganisms, absence of O, presence of an energy source (usually decomposable organic matter), and soil temperatures sufficient for anaerobic microbial activity. Couto et al. (1985), proposed that the lack of an energy source for microbial activity at depths below 40 cm was the most important factor preventing Fe reduction in some Oxisols in Brazil. In submerged soils, dissolution of Fe(III) oxides by microbial reduction starts as soon as O, nitrate, and Mn(IV) have been reduced (Ponnamperuma, 1972). Munch and Ottow (1980) found that amorphous forms of iron oxides, rather than crystalline forms of iron oxides, were preferentially reduced by Fe-reducing bacteria.

The purpose of our study was to investigate the pathway for iron oxide transformation in the topo-

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sequence of Oxisols from the Central Plateau of Brazil previously studied by Macedo and Bryant (1987). Our approach was to subject soil material from the Bo horizon of a dystrophic, clayey Dark-Red Latosol (clayey, oxidic, isothermic Anionic Acrustox), having codominant hematitic and goethitic Fe mineralogy to a reducing environment and observe the effects on the hematite and goethite minerals. Populations of Fe-reducing microorganisms indigenous to the soils were enhanced by modifying the soil environment. Subsequent changes in Fe mineralogies were attributed to the naturally occurring organisms present in these soils. Identification of the organisms and exact mechanisms of Fe reduction in soil environments are beyond the scope of this study.

MATERIALS AND METHODS

Selected Soil

The soil selected for use in this study belongs to a hydrosequence crossing a tableland located on the EMBRAPA-CPAC (Cerrado Agricultural Research Center) research station in the Central Plateau of Brazil (Fig. 1). Uniform clayey Tertiary/Quaternary sediments are the parent material for soil development throughout the hydrosequence. The well-drained and moderately well-drained soils in the hydrosequence, which are of primary importance in this study, are Anionic Acrustox, clayey, oxidic, isothermic, and the poorly drained soil is a Plinthic Acraquox, clayey, oxidic, isothermic (Soil Survey Staff, 1987). In the Brazilian classification system, the well-drained soils are Dark-Red Latosols, dystrophic, clayey; the moderately well-drained soils are Red-Yellow Latosols, dystrophic, clayey; and the poorly drained soil is a Hydromorphic Laterite, dystrophic, clayey (EMBRAPA, 1978).

Soil morphology, mineralogy, hydrology, landform relations and characterization data from this hydrosequence are presented in Macedo (1986), and Macedo and Bryant (1987). Kaolinite, quartz, gibbsite, and iron oxides are the dominant minerals in these soils; anatase, corundum, and rutile were detected in smaller amounts. A comparison of the mineralogies of the Dark-Red Latosol, which has 2.5YR hues throughout the profile, and the Red-Yellow Latosol, which has 10YR hues in the upper horizons and 2.5YR hues in the lower horizons of the profile, showed no difference in the mineral assemblages except for the iron oxides. Hematite and goethite were detected by x-ray diffraction throughout the profile of the Dark-Red Latosol and in the lower 2.5YR horizons of the Red-Yellow Latosol, whereas goethite is the only iron oxide mineral in the upper 10YR horizons of the Red-Yellow Latosol. Soil material from the Bo1 horizon (66–122-cm depth) of the well-drained member of the hydrosequence (Dark-Red Latosol, site A) was selected for use in the Fe reduction experiment of our study.

Microbial Reduction Experiment

The microbial reduction experiment was conducted in the laboratory at 25 °C. Eleven 32-mm diam. plexiglass cylinders were cut to 120-mm lengths, and rubber stoppers were placed at both ends of the cylinders. A drain tube with a stopcock was inserted in the bottom and both a funnel and a respirator tube were inserted in the top. Fine soil (<2-mm fraction) from the selected horizon was air-dried, and 30-g subsamples were placed into the cylinders over a filter (cotton or paper filter may be used) to prevent loss of soil through the drain tube. Soils were saturated with 50 mL of a 0.17 *M* sucrose solution. In order to continuously supply a source of energy for microorganism growth and remove the products of reduction, solutions were replaced at weekly intervals for a period of up to 1 yr. Changes in soil colors were also recorded.

One of the samples was saturated with deionized distilled water without sucrose and served as a control (sample A1). To further confirm the involvement of microbes in Fe reduction, another sample (A2) was gamma-irradiated (2.5 Mrad, for 12 h) in order to eliminate the natural population

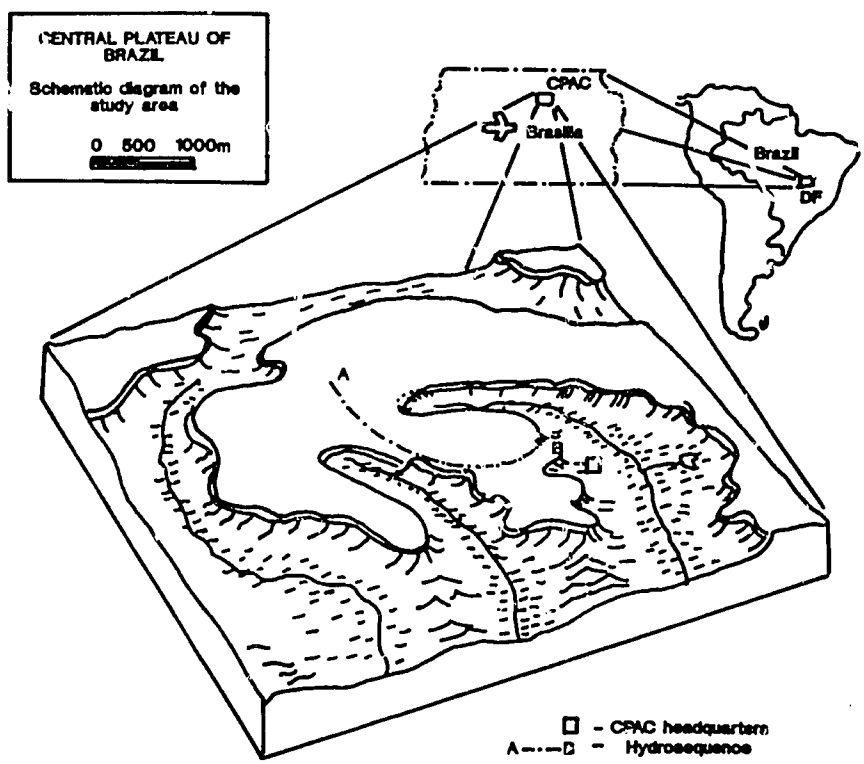

Fig. 1. Location of the study area in the Central Plateau of Brazil and block diagram of the location of the hydrosequence (A–B).

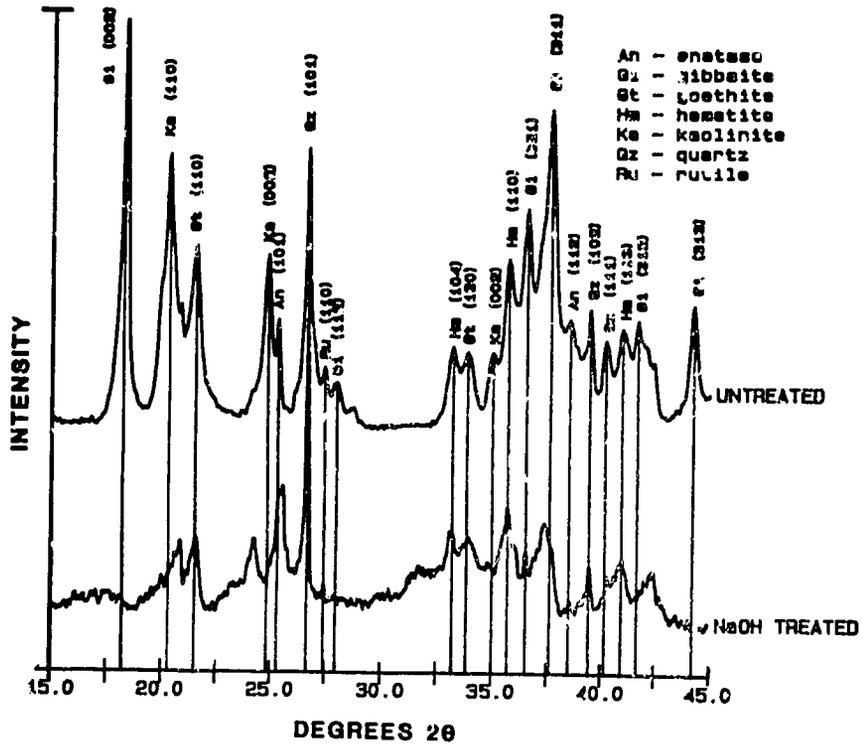

Fig. 2. X-ray diffraction pattern of the untreated and the NaOH-treated <2mm fraction of the Bo1 horizon from the Anionic Acrustox (Dark-Red Latosol, Site A).

of organisms in the soil (Cawse, 1975) before saturation with 0.17 *M* sucrose solution.

A time lag from 3 to 9 wk was necessary for the microbial population to increase to a level sufficient to start the reduction of Fe. The appearance of the first yellowish mottle in the samples was used as an indication of the beginning of iron oxide reduction. Reduction was selectively stopped in order to achieve a range in time lapse after the reduction had begun. Soil samples were subsequently dialyzed to eliminate excess sucrose and freeze-dried for storage.

Dry and moist colors of crushed and homogenized soil before and after the several reduction treatments were recorded using Munsell Soil Color Charts. A redness rating was determined according to the expression described by Hurst (1977): Redness rating = hue × chroma/value. In order to enhance the significance of the common colors for these soils which range from 10R to 10YR, numerical values representing hue were chosen as 5 for 10R, 4 for 2.5YR, 3 for 5YR, 2 for 7.5YR, and 1 for 10YR. Hue was interpolated between pages of the Mussell soil color charts as needed Numerical values for chroma and value are those of the Munsell notation.

Mineralogical Analyses

Following the described treatment, soil samples were ground down by means of an agate mortar to fractions < 0.25 mm for mineralogical analyses. X-ray powder diffraction (XRD) data were obtained using Ni-filtered CuK-α radiation (40 kV, 40 mA) with a 2θ compensating silt, a 0.2-mm-receiving slit, a diffracted beam graphite monochromator, and a scintillation detector. Powder mounts were prepared using a plexiglass holder by backfilling and then gently pressing the samples against hand ground slides (1000 grit) to minimize preferred orientation. Samples were step-scanned using a fixed counting time of 20 s/0.01 degrees 2θ. Data were acquired and analyzed on a microcomputer using commercially available software (ASYST ver. 2.0, Asyst Software Technologies, Inc., Rochester, NY). X-ray diffraction patterns were positioned with respect to a 3.343 Å d-spacing of the quartz d_{101} peak, which also gave correct spacings for anatase, rutile, and gibbsite. Patterns were interpreted using guidelines set forth by Brown and Brindley (1980) and by Brown (1980).

Iron oxides were concentrated in selected samples by treating with boiling 5 *M* NaOH for 60 min to remove 1:1 layer silicates and gibbsite (Norrish and Taylor, 1961; Kämpf and Schwertmann, 1982) prior to quantitative estimation by XRD. Iron oxides were extracted with Na-CBD (Fe_d) (Mehra and Jackson, 1960) and NH_4-oxalate (Fe_o) (USDA-Soil Conservation Service, 1972); extractable Fe and Al were determined by atomic adsorption. For making comparisons among samples from different treatments, XRD patterns were scaled in reference to the intensity of the quartz d_{101} peak.

RESULTS AND DISCUSSION

The Bo1 horizon (66–122 cm) of a Dark-Red Latosol was selected for this study because the mineral assemblage is typical for the highly weathered well-drained Oxisols of this area of the Central Plateau of Brazil and the organic matter content is low (<10 g kg^{-1} OC) so the energy source for microbial growth could be controlled by additions of sucrose solution. The total amount of Fe_d is 80 g kg^{-1} wherein hematite and goethite, at a ratio of approximately 0.4:0.6 as estimated by XRD, are the only crystalline iron oxides present. A low Fe_o/Fe_d ratio (0.02) in this sample further confirms that the iron oxides are mainly crystalline in nature (Schwertmann, 1959).

Figure 2 shows the XRD pattern of the untreated fraction <2 mm used in this experiment and that for the same sample after treatment with boiling 5 *M*

Table 1. Treatment duration, color, Fe_d and Al_d after microbial reduction of the <2-mm fraction of the Anionic Acrustox (Dark Red Latosol).

Sample no.	Saturation time	Reduction time	Mussell color	Redness rating	Fe_d	Al_d
	d		(moist)		g kg^{-1}	
Untreated	–	–	3.25YR 4/6	5.25	80	22
A1	360	–	3.25YR 4/6	5.25	78	22
A2	120	–	3.25YR 4/6	5.25	79	22
B	60	24	5YR 4/6	4.50	70	20
C	85	27	5YR 4/6	4.50	70	19
D	85	33	6.25YR 4/6	3.75	68	19
E	128	57	6.25YR 4/6	3.75	66	17
F	85	61	6.25YR 4/6	3.75	66	19
G	128	64	7.75YR 4/6	2.25	64	17
H	165	100	8.75YR 4/6	2.25	54	18
I	128	101	8.75YR 4/6	2.25	50	17
J	220	164	8.75YR 4/6	2.25	55	19
K	360	335	7.5YR 4/4	2.00	54	17

NaOH to remove kaolinite and gibbsite. The NaOH treatment had no effect on the peak positions of the resistant minerals or the iron oxide minerals, but peak intensities were enhanced. Peak positions for hematite are coincident with those reported for hematite with no apparent Al substitution (Joint Committee on Powder Diffraction Standard, 1974). Peak positions for goethite are shifted toward *d*-spacings lower than those reported for goethite, thus indicating a substitution of Al for Fe in the goethite lattice. Using the calculated *c* dimension (Schulze, 1984), the estimated amount of AlOOH substituting for FeOOH in the goethite in the soil used in this study is 34 mole %.

Microbial Reduction of Iron Oxides

The time table for the microbial reduction experiment is shown in Table 1. Saturation time is the total time that samples were kept under saturation with the 0.17 *M* sucrose solution (except for sample A1, which was saturated with deionized water only). Reduction time is the time that samples were under an "iron-reducing environment" as indicated by the appearance of the first yellow mottle. The Munsell color and redness ratings illustrate the resulting changes in the colors of the samples in relation to the time they were kept under reduction. Samples A1 and A2 showed no perceptible color change compared to an untreated sample. Samples B through K show a decrease in redness rating in accordance with increasing time under exposure to reducing conditions. The 7.5YR 4/4 color of sample K after treatment is frequently observed in the upper horizons of the Red Yellow Latosol from the hydrosequence.

The XRD patterns of an untreated sample in comparison with selected samples representing a range of microbial reduction of iron oxides are shown in Fig. 3. The results show that hematite was preferentially reduced and removed by microbial action as indicated by the decrease in the integrated areas under the d_{104}, d_{110}, and d_{113} peaks of hematite, whereas the d_{110} and d_{130} peaks of Al-substituted goethite remained unchanged.

The amount of Fe_d and Al_d remaining in the samples after the microbial reduction experiment was terminated are also shown in Table 1. The untreated sample indicates the total amount of Fe_d and Al_d orig-

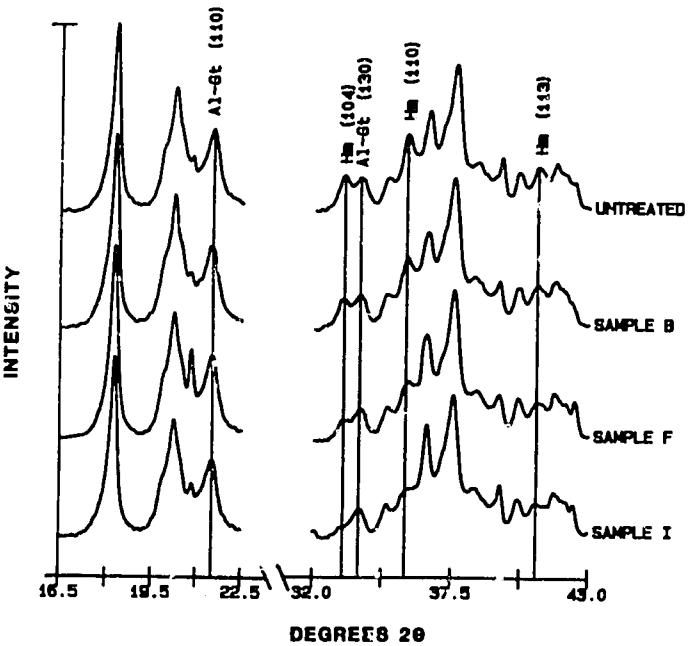

Fig. 3. X-ray diffraction pattern of an untreated sample of the < 2mm fraction of the Bo1 horizon of the Anionic Acrustox (Dark-Red Latosol), compared to patterns of selected samples representing a range in microbial reduction of iron oxides.

inally present in the samples. Values for samples B through K indicate that Fe reduction and dissolution increased with respect to time under reducing conditions. However, the amount of Al present in the samples shows little change with respect to increasing time under conditions of microbial reduction. Whereas no Al-substitution was detected in the hematite, and 34 mole % AlOOH substitutes in the goethite, these results further substantiate our conclusion that the iron oxide mineral attacked by microbial reduction was hematite.

The fact that no microbial growth and no evidence of Fe reduction was observed in a sample low in OC and saturated for a long period with distilled water without sucrose (sample A1) indicates that when a source of energy is absent, Fe reduction does not occur. In addition, the soil sample which had the natural microbial population destroyed by gamma irradiation (sample A2) showed no reduction of iron oxides despite saturation with a 0.17 *M* sucrose solution. These results suggest that the reduction observed in this experiment was microbial.

SUMMARY AND CONCLUSIONS

Analyses of x-ray diffractograms of samples subjected to microbial reduction indicate a preferential reduction of hematite over Al substituted goethite. Redness rating of the soil samples which underwent reduction decreased in relation to increasing duration of the reducing conditions. Determination of the amount of Fe and Al extracted during the reduction experiments further confirmed the preferential microbial reduction and dissolution of hematite over Al-substituted goethite.

As reported in other studies of natural environments (Torrent et al., 1980; Peña and Torrent, 1984; and Schwertmann, 1985), Al-substitution in the soil

goethite of this study is greater than in the coexisting hematite (34 mole % AlOOH in goethite and no apparent Al-substitution in hematite). Torrent et al. (1987) reported that reductive dissolution rates of synthetic hematites and goethites by Na-dithionite both decreased with increasing Al-substitution. Other factors, such as crystallinity, particle size, surface roughness, etc., that may influence the relative resistance of these minerals to microbial reduction were not investigated in this study. It remains to be determined whether the greater stability of Al-goethite compared with hematite without foreign ion substitution is caused by mineral structure or by Al-substitution.

Implications for Soil Genesis

Results of these experiments in combination with those of the soil/geomorphic study reported by Macedo and Bryant (1987) support the hypothesis of preferential reduction of hematite in natural conditions where a seasonal rise of the water table supplies additional moisture to the upper organic matter rich layers of these Oxisols. In the section of the hydrosequence in which the microenvironment at the interface of fresh or decaying roots and the surrounding soil becomes periodically saturated for a period of time long enough to induce a lowering of the redox potential, Fe(III) from the hematite structure appears to act preferentially as an alternative electron acceptor for microbial respiration. The more soluble Fe(III) from the hematite structure appears to act preferentially as an alternative electron acceptor for microbial respiration. The more soluble Fe(II) then migrates to the lower portion of the profile and may reoxidize to form plinthite in the water table fluctuation zone. The latter process has not been demonstrated in our studies, but the iron oxide distribution data presented in Macedo and Bryant (1987) suggests that this may be the case.

Short periods of hematite reduction followed by soil bioturbation (activities of termites, earthworms, ants, etc., acting to homogenize the soils), appears to have been repeated over a long enough period of time to remove all hematite from the upper horizons of these seasonally wet soils. The net result is a Red-Yellow Latosol that contains Al-substituted goethite as the only iron oxide mineral in the upper 10YR horizons of the profile.

The time required for complete reduction and removal of hematite by microbial processes in the field certainly is expected to be much longer than that demonstrated in the laboratory. The combined results of this study and those from Macedo and Bryant (1987), however, suggest that the process of preferential reduction of hematite is occurring at rates fast enough to reflect the soil wetness conditions of the present topographic and climatic conditions.

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