Published September, 1999

DIVISION S-9—SOIL MINERALOGY

Color Identification of Iron Oxides and Hydroxysulfates: Use and Limitations

A. C. Scheinost* and U. Schwertmann

ABSTRACT

Colors are widely used to describe soil profiles but seldom to identify minerals. This study was conducted to determine whether color measurements with a colorimeter could be employed to identify Fe oxides and hydroxysulfates, either as monomineralic samples or in soils. We measured the color of 277 Fe oxide and hydroxysulfate mineral samples, as well as 309 soils and soil fractions. Discriminant analysis was employed to separate the minerals in three different color systems: CIE-Yxy, CIE-L*a*b*, and Munsell. Using the color of monomineralic samples, 100% of maghemites and jarosites could be correctly classified, 95% of goethites, 90% of feroxyhites, 84% of lepidocrocites, 83% of hematites, 56% of ferrihydrites, 50% of akaganéites, and 44% of schwertmannites. In soil samples, goethite (90% correct classifications) could be reliably distinguished from hematite–goethite mixtures (82% correct classifications), and from lepidocrocite–goethite mixtures (89%). The identification of ferrihydrites, akaganéites, and schwertmannites largely failed because of similar average colors and because of high color variability. Because the color variability is a mineral-intrinsic property rather than produced by errors of measurement, color is in principle unsuited for identifying ferrihydrites, akaganéites, and schwertmannites. However, color may be used to identify goethite, hematite, lepidocrocite, jarosite, maghemite, and feroxyhite with a relatively high reliability. The choice of color system is not crucial for this type of analysis.

Soil color has long been known to reflect Fe oxide composition and content. An increase in chroma is generally interpreted as increasing Fe oxide content. Likewise, Schwertmann (1993) explained how yellowish, orange, and reddish hues of soils are caused by Fe-bearing minerals including Fe oxides, hydroxides, oxyhydroxides, and hydroxysulfates. Even when organic matter darkens a soil, the yellowish hues of goethite can easily be distinguished from the reddish hues of hematite. Orange hues are often caused by ferrihydrite or lepidocrocite, whose identification are crucial in many soils because they indicate active or recent redox processes. These obvious color differences within soils have resulted in color being a fundamental means to delineate, classify, and sample soil units. The identification and selection of individual soil units is made possible by the eye's ability to discriminate even between small changes in color (Wyszecki and Stiles, 1982).

Qualitative and quantitative analysis of soil Fe oxides is of great pedological interest because Fe oxide content and mineralogy reflect duration and intensity of pedogenesis. In addition, Fe oxides greatly affect the adsorption capacity of soils with respect to oxyanions. Therefore, the knowledge of their spatial variability is crucial, for example, for the risk assessment of selenate and arsenate toxicity (Zhang and Sparks, 1990; Bowell, 1994) or for the site-adapted application of phosphate fertilizers (Torrent, 1987; Van der Zee et al., 1988; Scheinost and Schwertmann, 1995). Standard methods for the mineral analysis, such as x-ray diffraction (XRD) and selective dissolution of Fe oxides, are time-consuming, not very sensitive, and not suited for field evaluations.

The difficulties of the standard methods relative to the ease of identifying soil color has resulted in many attempts to predict the type and concentration of Fe oxides simply from Munsell color (Schwertmann, 1993; Cornell and Schwertmann, 1996). While substantial progress has been made in the identification and quantification of goethite and hematite in soils (Torrent et al., 1983; Barrón and Torrent, 1986; Scheinost and Schwertmann, 1995), much less is known about the color variability of other Fe minerals, and whether they can be reliably distinguished by color. Schwertmann and Lentze (1966) determined frequency distributions of the Munsell coordinates of 90 synthetic Fe oxides and 174 natural Fe oxide samples. The goethites were clearly separated from the hematites by hue, while goethites, lepidocrocites, and ferrihydrites had similar (natural samples) or overlapping hues (synthetic samples). The greater similarity of the natural samples was explained by the influence of other coloring soil components such as organic matter and Mn oxides.

Most studies on soil color employed the Munsell color system because of its ease of use, ready availability, and historical importance to soil science (Simonson, 1993). However, newer systems, like those created by the Commission Internationale d'Eclairage (CIE), may be better suited to represent a uniform color space, that is, a color space where the Euclidean differences between colors are equivalent to the human perception of those differences (Melville and Atkinson, 1985). Another advantage of these new systems is that they overcome the limitations of the Munsell color system's discrete color chips. Those limitations include:

1. The resolution of color assignments is limited by the resolution of the chips. Interpolation between chips is possible in principle, but difficult in prac-

---

Lehrstuhl für Bodenkunde, TU München-Weihenstephan, 85350 Freising, Germany. A.C. Scheinost current address: Dep. of Plant and Soil Sciences, Univ. of Delaware, Newark, DE 19717. Received 30 July 1998. *Corresponding author (scheinos@udel.edu).

Published in Soil Sci. Soc. Am. J. 63:1463–1471 (1999).

Abbreviations: CIE, Commission Internationale d'Eclairage; DRS, diffuse reflectance spectroscopy; Fe_d, dithionite-citrate-bicarbonate extractable Fe; Fe_o, acid oxalate extractable Fe; XRD, x-ray diffraction.

Table 1. Synthetic (syn) and natural (nat) Fe oxides and hydroxysulfates used in this study. x_{Al} gives the mole fraction of Al for Fe substitution, Al/(Al+Fe).

Fe oxide	Abbrev	Most frequent color	n	Formula	Origin	x_{Al}
Hematite†	Hem	Moderate reddish brown	59	α-Fe_2O_3	syn	0–0.16
Goethite‡	Goeth	Strong yellowish brown	82	α-FeOOH	syn	0–0.33
Lepidocrocite§	Lepid	Moderate orange	32	γ-FeOOH	syn	0–0.14
Ferrihydrite¶	Ferrih	Brownish orange	59	$Fe_5HO_8 \cdot 4H_2O$	nat, syn	
Akaganeite#	Akag	Strong brown	8	β-FeOOH	syn	
Schwertmannite#	Schw	Dark orange yellow	16	$Fe_8O_8(OH)_6SO_4$	nat, syn	
Feroxyhite††	Feroxy	Strong brown	10	δ-FeOOH	nat, syn	
Maghermite‡‡	Magh	Dark yellowish brown	7	γ-Fe_2O_3	syn	0–0.17
Jarosite#	Jaros	Grayish yellow	4	$MFe_3(OH)_6(SO_4)_2$	nat	

† Murad and Schwertmann (1986); Stanjek (1991); Torrent and Schwertmann (1987).
‡ Schulze and Schwertmann (1984); Schwertmann et al. (1985).
§ Carlson and Schwertmann (1990); Murad and Schwertmann (1984); Schwertmann and Wolska (1990).
¶ Carlson and Schwertmann (1981, 1987); Schwertmann and Fischer (1973); Schwertmann et al. (1982b); Schwertmann and Kämpf (1983).
# Bigham et al. (1990, 1996); Schwertmann et al. (1995).
†† Carlson and Schwertmann (1980).
‡‡ Taylor and Schwertmann (1974).

tice as it has to be done in a three-dimensional space.

2. Due to metamerism, the assignment of a color may depend on the light source that is often not standardized, and on the physiological properties of the observer's color receptors.
3. Differences in gloss and other surface properties between the chips and the soil may influence the assignment.

These three factors cause a substantial scattering of color coordinates when the colors are determined repeatedly by one observer, or by several observers (Post et al., 1993). The limitations can be eliminated by using a colorimeter, which is an instrument capable of providing both accurate and precise color data (Torrent and Barrón, 1993). Another alternative is to calculate the color from diffuse reflectance spectra (Fernandez and Schulze, 1987); however, compared with this method, measurements with a colorimeter are faster, cheaper, and can be carried out in the field.

The objective of this study was to expand the work of Schwertmann and Lentze (1966), by using colorimeter measurements and a larger sample collection than was previously available. In addition to pure, synthetic or natural, Fe oxide and hydroxysulfate minerals (277 samples), we examined the color of 309 soil samples containing goethite, hematite, or lepidocrocite. For the discrimination of the groups (minerals or soils) we employed stepwise discriminant analysis (Jennrich, 1977). This statistical method allows separation of groups in n-dimensional space (n = number of discriminating variables, here the three color coordinates). The effectiveness of discrimination is given by correct classifications. By exactly quantifying the effectiveness of discrimination, discriminant analysis also allowed evaluation of different color systems.

MATERIALS AND METHODS

The 277 monomineralic samples included nine minerals: the oxides hematite and maghemite; the oxyhydroxides goethite, lepidocrocite, akaganéite, feroxyhite, and ferrihydrite; the oxyhydroxysulfate schwertmannite, and the hydroxysulfate jarosite (Table 1). Common features of these minerals are their yellow to red color caused by electronic transitions between the 3d orbitals of Fe(III) (Sherman and Waite, 1985), and their occurrence in soils or surface waters (Cornell and Schwertmann, 1996). The samples were either produced in the laboratory (synthetic) or collected in the field (natural). The purity of the minerals was determined by step-counted XRD analysis. The mineral samples were also characterized by determining dithionite-citrate-bicarbonate extractable Fe (Fe_d) (Mehra and Jackson, 1960; Holmgren, 1967) and acid oxalate extractable Fe, (Fe_o) (Schwertmann, 1964). The larger mineral groups — goethite, hematite, lepidocrocite, and ferrihydrite — represented a wide variation in conditions of forma-

Table 2. Soils and soil fractions used in this study.

Soil fraction	N	Origin	Mean Fe_d†	Fraction	Reference
			%		
Soils with Goethite:					
	132	Bavaria, FRG	1.2	<2 mm	Martin (1988); Scheinost (1995)
	6	Nigeria	38.4	<2 mm and <2 μm	Zeese et al. (1994)
	3	Brazil	11.3	<2 μm	Kämpf (1981)
	6	South Africa	29.1	crusts, pipe stems	Schwertmann & Fitzpatrick (1977)
	7	New Caledonia	38.4	whole	Schwertmann & Latham (1986)
Soils with Hematite (and Goethite):					
	39	Brazil	8.8	<2 μm	Schwertmann & Kämpf (1984)
	4	Nigeria	31.6	whole	Zeese et al. (1994)
	8	Rhine Valley	4.5	<2 μm	Schwertmann et al. (1982a)
	26	New Caledonia	46.3	whole	Schwertmann & Latham (1986)
	37	Terre Rosse	5.5	<2 μm	Boero & Schwertmann (1989)
	14	Worldwide	42.8	<2 μm	Stanjek (1991)
Soils with Lepidocrocite (and Goethite):					
	27	South Africa	24.5	crusts, pipe stems	Schwertmann & Fitzpatrick (1977)

† The dithionite-soluble Fe (Fe_d) times 1.5 gives a rough estimate of the Fe oxide content.

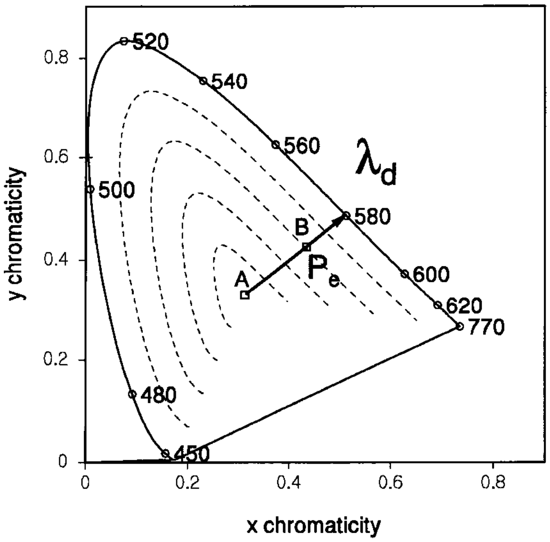

Fig. 1. Color designation in the CIE-Yxy system. Colors lie within the solid lines resembling a shoe sole. Colors within that plane may be given either by the Cartesian coordinates *x* and *y*, or by the dominant wavelength, λ_d (nm), and the excitation purity, P_e. The lightness, *Y*, is normal to the plane.

tion. A full range of Al for Fe substitution was included in the goethite, hematite, lepidocrocite, and maghemite samples (Table 1). The 309 soil samples were separated into three classes according to their Fe oxide mineral composition (Table 2). The relative mineral contents were determined by XRD using the untreated or the NaOH-treated clay fraction (Kämpf and Schwertmann, 1982a; 1982b), or by Mossbauer spectroscopy (Schwertmann et al., 1982a; 1982b; Murad and Schwertmann, 1988). The absolute Fe oxide contents were estimated from Fe_d and Fe_o.

Color of soils and monomineralic samples was measured with a model CR-300 Chroma Meter (Minolta, Osaka, Japan). This colorimeter uses a pulsed Xe light for a stable and uniform illumination of the sample. Three photocells measure the photons diffusely reflected by the sample through filters matching the CIE standard observer spectral response. We calibrated the colorimeter with a standard white plate (Minolta), and used an illumination type C (Commission Internationale d'Eclairage, 1978). In preparation for the color measurement, unfractionated soils, fine soils ($<$2 mm), and concretions were ground in an agate mortar until the color visually remained constant ($\approx$10 min; Torrent and Barrón, 1993). The monomineralic samples and the clay fractions of the soil samples, which had been freeze-dried from suspension, were used without further treatment. For the analysis, the head of the colorimeter (CR-A33a), which is protected by a glass window, was set onto the powdered samples. The pressure against the samples was standardized only by the weight of the head ($\approx$500 Pa). Less than 300 mg of sample was sufficient to cover the tube orifice (5 mm in diameter) with a thickness of at least 1 mm of sample. This thickness proved to be infinite with respect to visible radiation. After using the equipment for measuring hundreds of soil samples (not shown in this study), we observed scratches on the glass window protecting the sensor. Color measured through this scratched window deviated by $<$15% from color measured through a new window. Care was taken, therefore, to monitor a possible change with time. One goethite and one hematite sample were measured daily during the measuring period of 8 wk ($n = 37$). The color readings of these two samples were highly reproducible with standard deviations of $\leq$0.08 units of hue, $\leq$0.08 units of value, and $\leq$0.12 units of value. No systematic change of color with time was observed.

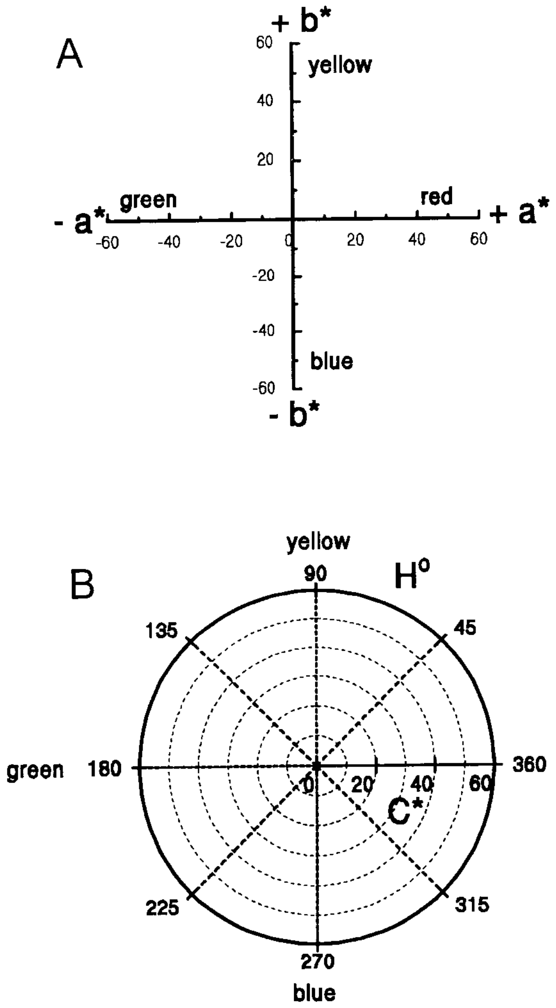

Fig. 2. Color designation in the CIE-L*a*b* system. A plane may be defined either (A) by *a and *b** in Cartesian notation or (B) by chroma (*C**) and hue (*H*°) in polar coordinates. The lightness axis, *L**, is normal to the plane.**

The digital output of the colorimeter, consisting of the mean tristimulus values X, Y, and Z of three replicated readings, was transmitted to a personal computer through the serial port. The tristimulus values were converted into the coordinates of three color spaces, CIE-Yxy, CIE-L*a*b*, and Munsell. For the conversion into the first two systems, equations were taken from Wyszecki and Stiles (1982). However, no closed equations exist to convert the tristimulus values into Munsell coordinates. The conversion was therefore accomplished by using a computer code (written by F. Billmeyer, Purdue University; see Fernandez and Schulze, 1987). This code utilizes the digitized tables of Wyszecki and Stiles (1982), and linearly interpolates between the discrete colors given there. The stepwise discriminant analysis was performed with the computer program package Statistica (StatSoft, 1996). The a priori classification probabilities of all groups (minerals or soils) were set to equal values to improve the discrimination of small groups (StatSoft, 1996).

Color Spaces

In the CIE-Yxy color space, all colors lie within a plane resembling a shoe sole (Fig. 1). An arbitrary point B within that plane is defined by the Cartesian coordinates *x* and *y*, where the redness increases with *x*, and the greenness increases with *y*. The lightness, *Y*, is perpendicular to *x* and *y* out of

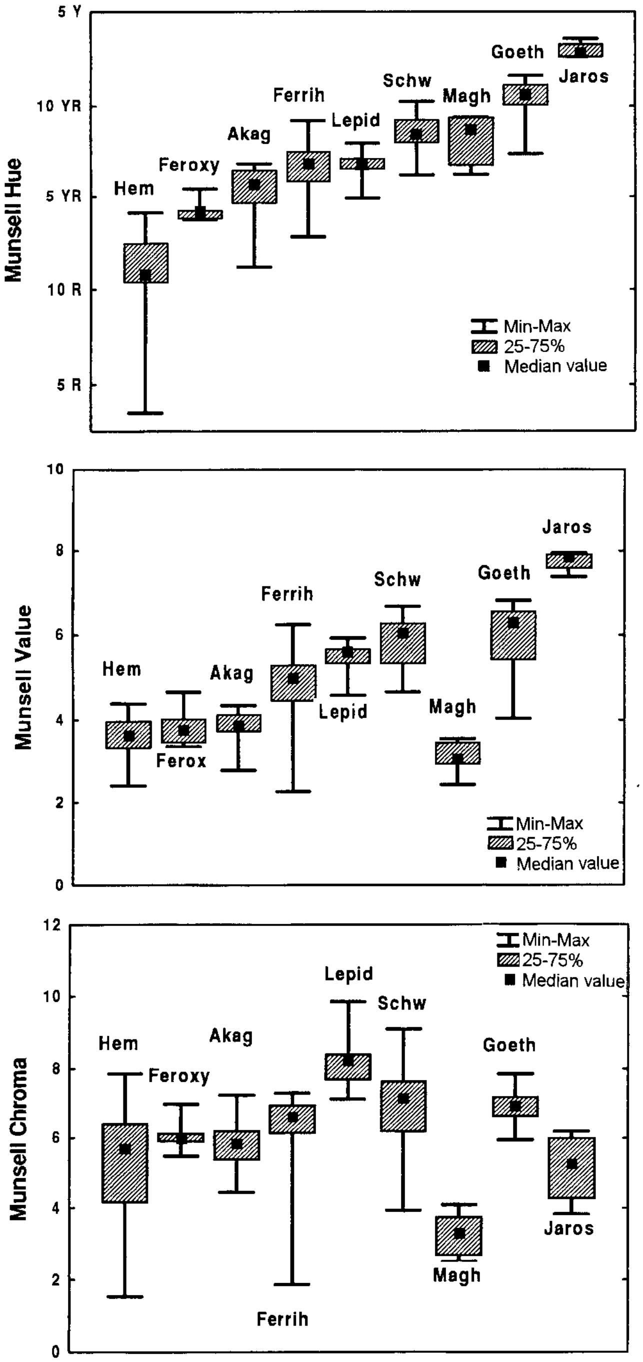

Fig. 3. Munsell coordinates of Fe oxides and hydroxysulfates.

the plane. An alternative way to define B is by drawing a line through B and the achromaticity point, A. The intersection of that centripetal line with the perimeter gives the dominant wavelength, λ_d, (580 nm for point B in Fig. 1). The relative distance between A and the intersection with the perimeter gives the excitation purity, P_e (0.6 for point B). The dominant wavelength is therefore similar to the hue, and P_e is similar to the chroma of the Munsell system.

In order to produce color systems with Euclidean distances similar to those perceived by the eye, a wide variety of so-called uniform color spaces have been developed (Hunter and Harold, 1987). We selected two of them, the Munsell system, because of its traditional usage in soil science (Simonson, 1993), and the CIE-L*a*b* system, because it is the most frequently used modern system (Commission Internationale d'Eclairage, 1978; Melville and Atkinson, 1985). A short description of the (among soil scientists) less well-known CIE-L*a*b* system is given in the following. Color planes are defined in this system by the Cartesian axes a^* and b^*, which coincide at the achromaticity point (Fig. 2A). The a^* axis extends to the complementary colors red ($+a^*$) and green ($-a^*$), and the b^* axis extends to the complementary colors yellow ($+b^*$) and blue ($-b^*$). A third axis normal to a^* and b^* defines the lightness, L^*. Alternatively, the Cartesian coordinates a^* and b^* may be replaced by the polar coordinates $H°$ (hue) and C^* (chroma), resulting in a cylindrical coordination system comparable to the standard notation of the Munsell color system (Fig. 2B). The Munsell system, in turn, may be converted into a Cartesian system using the rectangular axes x_M and y_M instead of hue and chroma (Melville and Atkinson, 1985).

Table 3. Munsell colors of the Fe oxides and hydroxysulfates (median and range).

	Hue	Value	Chroma	n
Hematite	1.2 YR (3.5 R–4.1 YR)	3.6 (2.4–4.4)	5.2 (1.5–7.9)	59
Goethite	0.4 Y (7.3 YR–1.6 Y)	6.0 (4.0–6.8)	6.9 (6.0–7.9)	82
Lepidocrocite	6.8 YR (4.9 YR–7.9 YR)	5.5 (4.6–5.9)	8.2 (7.1–9.9)	32
Ferrihydrite	6.6 YR (2.8 YR–9.2 YR)	4.9 (2.3–6.3)	6.3 (1.9–7.3)	59
Akaganéite	5.2 YR (1.2 YR–6.8 YR)	3.8 (2.8–4.3)	5.8 (4.4–7.3)	8
Schwertmannite	8.5 YR (6.2 YR–0.3 Y)	5.9 (4.7–6.7)	6.9 (4.0–9.1)	16
Feroxyhite	4.2 YR (3.7 YR–5.4 YR)	3.8 (3.4–4.7)	6.0 (5.5–7.0)	10
Maghemite	8.3 YR (6.2 YR–9.4 YR)	3.1 (2.5–3.6)	3.2 (2.5–4.1)	7
Jarosite	3.0 Y (2.6 Y–3.6 Y)	7.8 (7.4–8.0)	5.1 (3.8–6.2)	4

The expression of color in cylindrical coordinates is better suited for its visualization, and is therefore used in the following discussion whenever the color description is of importance. On the other hand, the polar coordinates are unsuited for multivariate statistical analyses, because hue and chroma do not represent Euclidean distances. Thus, only the Cartesian coordinates were used in statistical calculations.

RESULTS AND DISCUSSION

Color of Pure Iron Oxides and Hydroxysulfates

The hues of the samples studied extended from 3.5 R (hematite) to 3.6 Y (jarosite) (Fig. 3, Table 3). The Munsell value varied between 2.3 (ferrihydrite) and 8.0 (jarosite), the chroma between 1.5 (hematite) and 9.9 (lepidocrocite). Hematite was clearly distinguishable from goethite, because all hematite samples were redder than 4.1 YR, and all goethite samples were yellower than 7.3 YR (Table 3). The jarosites were yellower and higher in value than the goethites. The remaining Fe oxides filled the gap between the average hue of hematite and of goethite, and strongly overlapped with each other, making a distinction solely by hue impossible. The average hues of hematite, ferrihydrite and lepidocrocite were close to the ones given by Schwertmann and Lentze (1966), but the average hue of goethite was 2.5 units yellower. This difference may be explained by

Table 4. Comparison of the classification result for monomineralic samples in three color spaces.

	Yxy	CIE-L*a*b*	Munsell-$x_M y_M z_M$
	%†		
Hematite	**83**	**76**	**76**
Goethite	**95**	**88**	**85**
Lepidocrocite	**84**	**97**	**88**
Ferrihydrite	**56**	**54**	**54**
Akaganéite	**50**	**88**	**88**
Schwertmannite	**44**	**38**	**38**
Feroxyhite	**90**	**90**	**90**
Maghemite	**100**	**100**	**100**
Jarosite	**100**	**100**	**100**
all	**79**	**77**	**75**

† Percentage of correct classifications.

Table 5. Standardized coefficients for the canonical variables of monomineralic samples.

	Root 1	Root 2	Root 3
Y	**0.21**	**−1.28**	**0.09**
x	**1.05**	**−0.74**	**1.01**
y	**−1.45**	**0.77**	**0.01**
Cumulative probability	**0.88**	**0.96**	**1.00**

the more precise color determination or by the larger sample set of our study.

Both the red hue and the (correlated) low value of hematite are due to a strong absorption band at 530 nm (Scheinost et al., 1998). This band has been assigned to an electron pair transition fostered by the interaction of neighboring Fe atoms in face-sharing octahedra (Sherman and Waite, 1985). Other Fe oxides have both edge- and corner-sharing octahedra and hence larger Fe to Fe distances (Manceau and Combes, 1988). Consequently, the electron pair transition of these minerals is weaker (as shown for goethite by Scheinost et al., 1999), and the hues are more yellow than that of hematite. Jarosite has only corner-sharing octahedra and the largest Fe to Fe distances (Gaines et al., 1997). Therefore, the reflectance spectra of jarosite lack the electron pair transition band and show only the weak, spin-forbidden, 3d absorption bands of Fe(III) (Buckingham and Sommer, 1983). The resulting weak absorption across the visible range is responsible for the grayish-yellow color of jarosite (Fig. 3). The strong correlation between value and yellowness ($r = 0.95$ without maghemite, Fig. 3) may be explained by both the stronger electron pair transition bands of hematite and feroxyhite and by the brighter appearance of yellow colors (Hunter and Harold, 1987). Maghemite has a much lower value than would be expected from its hue (and its structure). This low value is caused by a broad Fe^{2+} to Fe^{3+} charge transfer band that centers at 1500 nm and drastically reduces the reflectance in the visible range (Scheinost et al., 1998).

Applying the discriminant analysis, the best separation of the mineral samples was achieved in the CIE-Yxy space (79% of all samples correctly classified), followed by the CIE-L*a*b* space (77%), and the (Cartesian) Munsell system (75%) (Table 4). To check if this ranking was significant, we repeated the calculation for randomly selected data subsets. The classification results using the CIE-Yxy and the CIE-L*a*b* systems were always better than those by the Munsell system; however, the difference between the systems never exceeded 5%, and the distribution of correct classifications among the classes was always similar. This suggests that the choice of the color system is not crucial for the discrimination of the minerals. In the following, results will be shown for the CIE-Yxy system only.

The discrimination was based on three discriminant functions, or roots (Table 5). The first root achieved 88% of the final discrimination, the second root added another 8%, and the third root the remaining 4% (see cumulative probabilities in Table 5). All three roots were statistically significant. The standardized canonical variables show the relative contributions of the discriminating variables (i.e., the color coordinates) to the roots. The first and most important root is dominated by x and y, indicating that the discrimination result depends largely on these two variables corresponding with hue and chroma in the cylindrical coordination system. The minor importance of Y (or value) is probably due to the high correlation between hue and value (see above).

The dark yellowish brown maghemites and the grayish-yellow jarosites were perfectly classified (Table 6). Goethite, hematite, lepidocrocite, and feroxyhite were also successfully (though not perfectly) classified. However, ferrihydrite, akaganéite, and schwertmannite samples were only partly separated from each other (Table 6). The dependable discrimination of maghemite and jarosite is in line with their isolated location in the color space (Fig. 3), which, in turn, is due to the unique causes of their color (see above). Hematite samples have the reddest average hue, but the wide range in hue causes a slight overlap with feroxyhite. Goethites, with the yellowest hues (besides jarosite), interfere with the neighboring schwertmannites due to a relatively high variability in hue. The good classification result for the

Table 6. Classification result for monomineralic samples based on *Yxy* color coordinates.†

	Correct	Hem	Goeth	Lepid	Ferrih	Akag	Schw	Feroxy	Magh	Jaros
	%									
Hematite	**83**	**49**	**0**	**0**	**0**	**0**	**0**	**9**	**1**	**0**
Goethite	**95**	**0**	**78**	**0**	**2**	**0**	**2**	**0**	**0**	**0**
Lepidocrocite	**84**	**0**	**0**	**27**	**2**	**0**	**2**	**1**	**0**	**0**
Ferrihydrite	**56**	**1**	**0**	**0**	**33**	**9**	**12**	**2**	**2**	**0**
Akaganéite	**50**	**1**	**0**	**0**	**2**	**4**	**0**	**1**	**0**	**0**
Schwertmannite	**44**	**0**	**5**	**0**	**4**	**0**	**7**	**0**	**0**	**0**
Feroxyhite	**90**	**0**	**0**	**0**	**0**	**1**	**0**	**9**	**0**	**0**
Maghemite	**100**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**7**	**0**
Jarosite	**100**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**4**
all	**79**	**51**	**83**	**27**	**43**	**14**	**23**	**22**	**10**	**4**

† Rows, observed classifications; columns, predicted classifications.

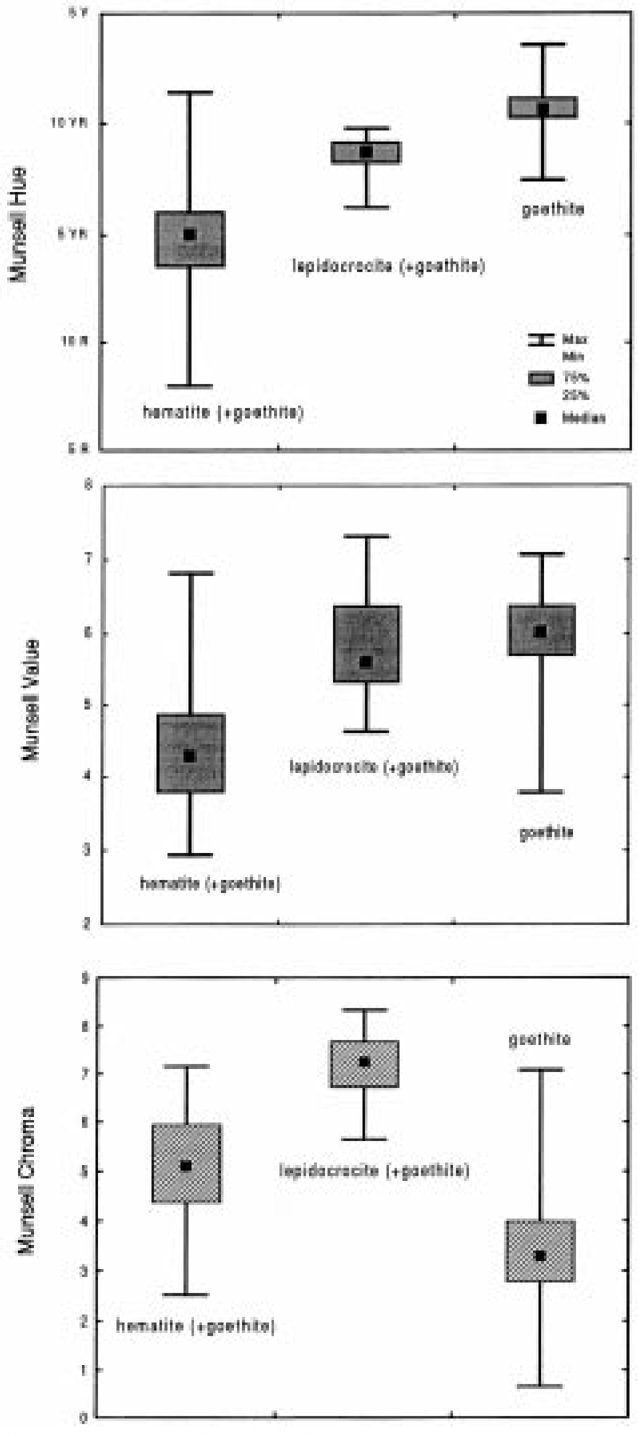

Fig. 4. Munsell coordinates of soils.

intermediate colors of lepidocrocite and feroxyhite is because of their low variability in hue and value. In contrast, intermediate color together with high variability leads to the poor classification results for ferrihydrite, akaganéite, and schwertmannite. Thus, the discrimination of the minerals with a similar cause of color (weak electron pair transition by edge- and corner-sharing octahedra) depends strongly on their variability.

Color variation within a given mineral form has been explained by several reasons. For example, the color of hematite changed from yellow-red to blue-red as the diameter of crystals increased from 0.1 to 1.0 μm (Schwertmann, 1993). A similar effect is caused by the aggregation of hematite crystals (Torrent and Schwertmann, 1987). Barrón and Torrent (1984) found a positive correlation between Munsell value and the Al substitution of hematite. Goethite and akaganéite crystals appear darker as their size decreases (Schwertmann, 1993). Acicular hematite crystals have a more yellow hue than hexagonal hematite crystals (Hund, 1981). For the goethite samples of our study, relations between morphology and color have been investigated and published (Scheinost et al., 1999). In line with former results, the goethite samples increased in darkness and redness as the needle length decreased from 0.8 to 0.05 μm. The variation in needle length, in turn, was caused by either Al substitution or temperature of crystallization (Scheinost et al., 1999). Parameters like crystal size and shape, particle aggregation, Al substitution, or other impurities may also be responsible for the observed color variability of the other minerals, but have not been investigated. Moreover, transition metal for Fe substitution also greatly affects color by giving rise to additional crystal-field bands (Schwertmann, 1993; Scheinost and Schwertmann, 1997). However, because of their relative rareness in nature, samples with transition metal for Fe substitution were not included in our study, and are not responsible for the variability of the data presented here.

Color of Soils and Soil Fractions

The hue of goethitic soils was close to the hue of synthetic goethites (compare Fig. 3 with Fig. 4, and Table 3 with Table 7). Soils containing both hematite and goethite had hues between those of the pure hematite and goethite samples, and soils containing both lepidocrocite and goethite had hues between those of the pure lepidocrocite and goethite minerals. Thus, the hue of soils is largely determined by these three Fe oxides. Value and chroma of soils were substantially lower than those of the pure minerals. This is due to the reduction of value by soil organic matter, and the reduction of chroma by the dilution of the Fe oxide pigments with the soil matrix, which usually consists of minerals of high reflectance (Fernández and Schulze, 1992; Scheinost and Schwertmann, 1995). Nevertheless, the red hematitic soils were darker than goethitic soils in accordance with results for the pure minerals, confirming that not only soil organic matter but also Fe oxide minerals strongly influence the value. Similarly, the high chroma of lepidocrocite-containing soils is in line with the high chroma of pure lepidocrocite. In addition, the significantly higher Fe oxide content of soils with lepidocrocite or hematite may contribute to their higher chroma (Table 2).

The result of the discriminant analysis for the soil samples is shown in Table 8. About 90% of the soil samples were correctly classified using the CIE-Yxy coordinates (results were similar for the other two color systems). This discrimination is surprisingly successful

Table 7. Munsell colors of soil samples (median and range).

	Goethite	Hematite (+Goethite)†	Lepidocrocite (+Goethite)‡
n	**159**	**107**	**27**
Hue	**0.6 Y** **(7.4 YR–3.5 Y)**	**4.7 HR** **(8.0 R–1.4 Y)**	**8.6 YR** **(6.2 YR–9.8 YR)**
Value	**5.9** **(3.8–7.1)**	**4.3** **(2.3–6.8)**	**5.8** **(4.6–7.3)**
Chroma	**3.5** **(0.7–7.1)**	**5.2** **(2.5–7.2)**	**7.2** **(5.6–8.3)**
Fe oxides, g g^{-1}	**8.7** **(0–88.1)**	**29.7** **(2.7–83.4)**	**34.5** **(5.0–74.0)**
Fraction of hematite† or lepidocrocite‡, respectively		**0.58** **(0.05–1.00)**	**0.49** **(0.05–1.00)**

† Hematite/(Hematite + Goethite) ≥0.05 mol mol^{-1}.
‡ Lepidocrocite/(Lepidocrocite + Goethite) ≥0.05 mol mol^{-1}.

if one takes into account that (i) the color of soils is influenced by additional color-bearing and colorless components, and (ii) most of the samples classified as hematite or lepidocrocite soils contain a substantial amount of goethite. The positive result may be explained by the clear separation of goethite and lepidocrocite by chroma, and by the pronounced red shift of soils by even small relative amounts of hematite (Fig. 5).

Soils dominated by Fe minerals other than goethite, hematite, and lepidocrocite were not available for this study. Nevertheless, conclusions on the identification of these other Fe oxides in soils may be drawn from the results of the pure minerals. The unique color of jarosite should always allow for a reliable determination of acid sulfate soils (Fanning et al., 1993). In contrast, the unique (among Fe oxides) color of maghemite is similar to that of Mn oxides and soil organic matter, which may prevent the identification of maghemite in soils. The combination of color and simple field tests (e.g., a magnet for detecting maghemite and magnetite, H_2O_2 for detecting Mn oxides) or the use of diffuse reflectance spectroscopy (DRS) may allow for an unequivocal identification of maghemite. However, there is little chance that the other minerals (schwertmannite, ferrihydrite, akaganéite and feroxyhite) may be detected in soils unless they would occur in substantial quantities and separated from other Fe oxides (e.g., in concretions).

Comparison with Diffuse Reflectance Spectroscopy

The color of minerals is directly related to their wavelength-dependent reflectance of visible light. Therefore, our results are directly comparable with those of a related paper where second-derivative DRS was employed to identify pure Fe oxides and Fe oxides in soils (Scheinost et al., 1998). The mineral samples were better discriminated by color coordinates than by absorption band positions (88 vs. 66% correct classifications). Furthermore, soils containing lepidocrocite and goethite could be reliably discriminated from goethitic soils by color, while the absorption band positions did not allow for discriminating them. That means that color coordinates are more sensitive to small spectral changes than band positions. Only hematite and maghemite have band positions that are clearly separated from those of the other Fe oxides. Therefore, second-derivative DRS is more sensitive in detecting these two Fe oxides than color. In conclusion, band positions and color together offer a more reliable identification of Fe oxides in soils than one of the parameters alone. Because both parameters can be derived from diffuse reflectance spectra, spectrometers offer improved discriminations compared with colorimeters, but are much more expensive.

Table 8. Classification result for soil samples based on CIE-Yxy coordinates.†

Soils with	Correct	Goethite	Hematite (+Goethite)	Lepidocrocite (+Goethite)
	%			
Goethite	90	143	2	14
Hematite (+Goethite)	82	18	94	2
Lepidocrocite (+Goethite)	89	1	2	25
Total	87	162	98	41

† Rows give the observed classifications and columns the predicted classifications.

Classification of Samples with Unknown Composition

Classification functions derived by discriminant analysis allow classification of unknown samples. For this, one has to multiply the color coordinates of each sample by the factors given in Table 9 (for pure Fe oxides or hydroxysulfates) or Table 10 (for soils). The sum of each row (including the constant) will give the scores

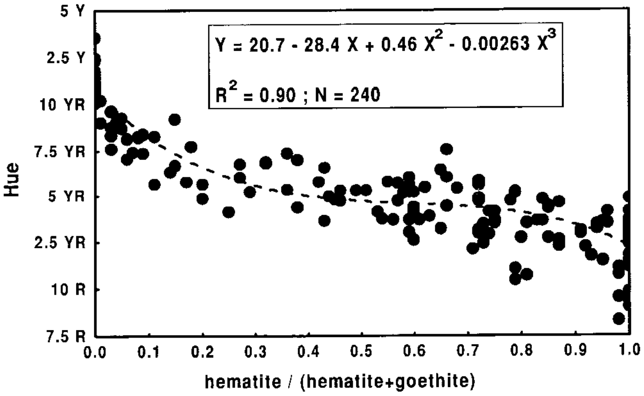

Fig. 5. Hue of hematitic soils as a function of the relative hematite content.

Table 9. Coefficients of the classification functions for monomineralic samples, based on CIE-Yxy coordinates.

	Multiply with			
	Y	*x*	*y*	Constant
Hematite	−2.63	−657	4627	−662
Goethite	−2.99	−1064	5812	−931
Lepidocrocite	−2.74	−841	5375	−860
Ferrihydrite	−2.95	−901	5373	−827
Akaganéite	−3.07	−838	5227	−797
Schwertmannite	−2.79	−954	5514	−863
Feroxyhite	−2.90	−758	5048	−768
Maghemite	−3.61	−1101	5596	−817
Jarosite	−1.82	−913	5210	−799

Table 10. Coefficients of the classification functions for soil samples, based on CIE-Yxy coordinates.

	Multiply with			
	Y	*x*	*y*	Constant
Goethite	0.436	−229	2202	−373
Hematite (+Goethite)	0.383	−65	1998	−363
Lepidocrocite (+Goethite)	0.575	−122	2247	−441

for each class. The unknown sample is most probably the mineral or soil which yields the highest scores. However, one has to keep in mind the limitations of the method as revealed by the correct classifications (Table 6, Table 8).

CONCLUSION

Goethite, akaganéite, and hematite samples are clearly separated by hue. Maghemites and jarosites can be distinguished by their extreme values, and lepidocrocites mainly by their high chromas. The other minerals with intermediate hues, values, and chromas — namely feroxyhite, ferrihydrite and schwertmannite — cannot be reliably identified by their color. Their discrimination is restricted, on one hand, by the similarity in color, which can be explained by similar Fe to Fe distances in the crystal structure. On the other hand, these minerals have a large color variability due to variation in particle size and shape, particle aggregation, crystal defects, or impurities, which further inhibits their classification based on color. Soils containing hematite or lepidocrocite can be reliably discriminated from soils containing only goethite, even when their Fe oxide composition is dominated by goethite. In addition, jarosite, feroxyhite, and maghemite may be identified in soils. However, it is unlikely that color can be used to identify ferrihydrite, akaganéite, and schwertmannite in soils.

ACKNOWLEDGMENTS

We are deeply indebted to J.M. Bigham (Ohio State Univ.), D. Laird (USDA-ARS), and D.G. Schulze (Purdue Univ.) for their help with improving a first version of the manuscript. D.G. Schulze provided the computer code to calculate Munsell colors. This study was funded by the Deutsche Forschungsgemeinschaft.

REFERENCES

Barrón, V., and J. Torrent. 1984. Influence of aluminium substitution on the color of synthetic hematites. Clays Clay Miner. 32:157–158.

Barrón, V., and J. Torrent. 1986. Use of the Kubelka-Munk theory to study the influence of iron oxides on soil colour. J. Soil Sci. 37:499–510.

Bigham, J.M., U. Schwertmann, L. Carlson, and E. Murad. 1990. A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters. Geochim. Cosmochim. Acta 54:2743–2758.

Bigham, J.M., U. Schwertmann, and G. Pfab. 1996. Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. Appl. Geochem. 11:845–852.

Boero, V., and U. Schwertmann. 1989. Iron oxide mineralogy of Terra Rossa and its genetic implications. Geoderma 44:319–327.

Bowell, R.J. 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. Appl. Geochem. 9:279–286.

Buckingham, W.F., and S.E. Sommer. 1983. Mineralogical characterization of rock surfaces formed by hydrothermal alteration and weathering — Application to remote sensing. Econ. Geol. 78: 664–674.

Carlson, L., and U. Schwertmann. 1980. Natural occurrence of feroxyhite (δ-FeOOH). Clays Clay Miner. 28:272–280.

Carlson, L., and U. Schwertmann. 1981. Natural ferrihydrites in surface deposits from Finland and their association with silica. Geochim. Cosmochim. Acta 45:421–429.

Carlson, L., and U. Schwertmann. 1987. Iron and manganese oxides in Finnish ground water treatment plants. Water Res. 21:165–170.

Carlson, L., and U. Schwertmann. 1990. The effect of CO_2 and oxidation rate on the formation of goethite versus lepidocrocite from an Fe(II) system at pH 6 and 7. Clay Miner. 25:65–71.

Commission Internationale d'Eclairage. 1978. Recommendations on uniform color spaces, color difference and psychometric color terms. Colorimetry, Suppl. 2 to Publ. 15. CIE, Paris.

Cornell, R.M., and U. Schwertmann. 1996. The iron oxides: Structure, properties, reactions, occurrence and uses. VCH Verlagsgesellschaft, Weinheim.

Fanning, D.S., M.C. Rabenhorst, and J.M. Bigham. 1993. Colors of acid sulfate soils. p. 91–108. *In* J.M. Bigham and E. Ciolkosz (ed.) Soil color. SSSA Spec. Publ. 31. SSSA, Madison, WI.

Fernandez, R.N., and D.G. Schulze. 1987. Calculation of soil color from reflectance spectra. Soil Sci. Soc. Am. J. 51:1277–1282.

Fernández, R.N., and D.G. Schulze. 1992. Munsell colors of soils simulated by mixtures of goethite and hematite with kaolinite. Z. Pflanzenernaehr. Bodenkd. 155:473–478.

Gaines, R.V., H.C.W. Skinner, E.E. Foord, B. Mason, and A. Rosenzweig. 1997. Dana's new mineralogy. John Wiley & Sons, New York.

Holmgren, G.G.S. 1967. A rapid citrate-dithionite extractable iron procedure. Soil Sci. Soc. Am. Proc. 31:210–211.

Hund, F. 1981. Inorganic pigments: Basis for coloured, uncoloured and transparent properties. Angew. Chem. Int. Ed. Eng. 20:723–730.

Hunter, R.S., and R.W. Harold. 1987. The measurement of appearance. John Wiley & Sons, New York.

Jennrich, R.I. 1977. Stepwise discriminant analysis. p. 130–174. *In* K. Enslein et al. (ed.) Statistical methods for digital computers. John Wiley & Sons, New York.

Kämpf, N., 1981. Die Eisenoxidmineralogie einer Klimasequenz von Böden aus Eruptiva in Rio Grande Do Sud, Brasilien. Diss. thesis. Technische Universität München, Freising, Germany.

Kämpf, N., and U. Schwertmann. 1982a. The 5-*M*-NaOH concentration treatment for iron oxides in soils. Clays Clay Miner. 30:401–408.

Kämpf, N., and U. Schwertmann. 1982b. Quantitative determination of goethite and hematite in kaolinitic soils by x-ray diffraction. Clay Miner. 17:359–363.

Manceau, A., and J.M. Combes. 1988. Structure of Mn and Fe oxides and oxyhydroxides: A topological approach by EXAFS. Phys. Chem. Miner. 15:283–295.

Martin, W., 1988. Die Erodierbarkeit von Böden unter simulierten und natürlichen Regen und ihre Abhängigkeit von Bodeneigenschaften. Ph.D. thesis. Technische Universität München, Freising, Germany.

Mehra, O.P., and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Miner. 7:317–327.

Melville, M.D., and G. Atkinson. 1985. Soil colour: Its measurement and its designation in models of uniform colour space. J. Soil Sci. 36:495–512.

Murad, E., and U. Schwertmann. 1984. The influence of crystallinity on the Mössbauer spectrum of lepidocrocite. Mineral. Mag. 48:507–511.

Murad, E., and U. Schwertmann. 1986. Influence of Al substitution and crystal size on the room-temperature Mössbauer spectrum of hematite. Clays Clay Miner. 34:1–6.

Murad, E., and U. Schwertmann. 1988. The characterization of poorly crystalline Si-containing natural iron oxides by Mössbauer spectroscopy. Hyperfine Interact. 41:835–838.

Post, D.F., S.J. Levine, R.B. Bryant, M.D. Mays, A.K. Batchily, R. Escadafal, and A.R. Huete. 1993. Correlations between field and laboratory measurements of soil color. p. 35–49. *In* J.M. Bigham and E. Ciolkosz (ed.) Soil color. SSSA Spec. Publ. 31. SSSA, Madison, WI.

Scheinost, A.C. 1995. Pedotransfer-Funktionen zum Wasser- und Stoffhaushalt einer Bodenlandschaft. FAM-Bericht, 6. Shaker-Verlag, Aachen, Germany.

Scheinost, A.C., A. Chavernas, V. Barrón, and J. Torrent. 1998. Use and limitations of second-derivative diffuse reflectance spectroscopy to identify and quantify Fe oxides in soils. Clays Clay Miner. 46:528–536.

Scheinost, A.C., D.G. Schulze, and U. Schwertmann. 1999. Diffuse reflectance spectra of Al substituted goethite: A ligand field approach. Clays Clay Miner. 47:156–164.

Scheinost, A.C., and U. Schwertmann. 1995. Predicting phosphate adsorption–desorption in a soilscape. Soil Sci. Soc. Am. J. 59:1575–1580.

Scheinost, A.C., and U. Schwertmann. 1997. VIS-NIR reflectance spectra of goethite (α-FeOOH) as a function of particle size, unit-cell size, and cation substitution. Lunar and Planetary Science XXVIII. Lunar and Planetary Inst., Houston, TX.

Schulze, D.G., and U. Schwertmann. 1984. The influence of aluminium on iron oxides: X. Properties of Al-substituted goethites. Clay Miner. 19:521–529.

Schwertmann, U. 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. Z. Pflanzenernaehr. Dueng. Bodenkd. 105:194–202.

Schwertmann, U. 1993. Relations between iron oxides, soil color and soil formation. p. 51–69. *In* J.M. Bigham and E.J. Ciolkosz (ed.) Soil color. SSSA Spec. Publ. 31. SSSA, Madison, WI.

Schwertmann, U., J.M. Bigham, and E. Murad. 1995. The first occurrence of Schwertmannite in a natural stream environment. Eur. J. Mineral. 7:547–552.

Schwertmann, U., P. Cambier, and E. Murad. 1985. Properties of goethites of varying crystallinity. Clays Clay Miner. 33:369–378.

Schwertmann, U., and W.R. Fischer. 1973. Natural "amorphous" ferric hydroxide. Geoderma 10:237–247.

Schwertmann, U., and R.W. Fitzpatrick. 1977. Occurrence of lepidocrocite and its association with goethite in Natal soils. Soil Sci. Soc. Am. J. 41:1013–1018.

Schwertmann, U., and N. Kämpf. 1983. Óxidos de ferro jovens em ambientes pedogenéticos brasileiros. Rev. Bras. Ci. Solo 7:251–255.

Schwertmann, U., and N. Kämpf. 1984. Properties of goethite and hematite in kaolinitic soils of southern and central Brazil. Soil Sci. 139:344–350.

Schwertmann, U., and M. Latham. 1986. Properties of iron oxides in some New Caledonian soils. Geoderma 39:105–123.

Schwertmann, U., and W. Lentze. 1966. Bodenfarbe und Eisenoxidform. Z. Pflanzenernaehr. Dueng. Bodenkd. 115:209–214.

Schwertmann, U., E. Murad, and D.G. Schulze. 1982a. Is there Holocene reddening (hematite formation) in soils of axeric temperate areas? Geoderma 27:209–223.

Schwertmann, U., D.G. Schulze, and E. Murad. 1982b. Identification of ferrihydrite in soils by dissolution kinetics, differential x-ray diffraction, and Moessbauer spectroscopy. Soil Sci. Soc. Am. J. 46:869–875.

Schwertmann, U., and E. Wolska. 1990. The influence of aluminum on iron oxides: XV. Al-for-Fe substitution in synthetic lepidocrocite. Clays Clay Miner. 38:209–212.

Sherman, D.M., and T.D. Waite. 1985. Electronic spectra of Fe3+ oxides and oxide hydroxides in the near IR to near UV. Am. Mineral. 70:1262–1269.

Simonson, R.W. 1993. Soil color standards and terms for field use — History of their development. p. 1–20. *In* J.M. Bigham and E.J. Ciolkosz (ed.) Soil color. SSSA Spec. Publ. 31. SSSA, Madison, WI.

Stanjek, H., 1991. Aluminium- und Hydroxylsubstitution in synthetischen und natürlichen Hämatiten. Ph.D. thesis. Technische Universität München, Freising, Germany.

StatSoft. 1996. Statistica for Windows. StatSoft, Tulsa, OK.

Taylor, R.M., and U. Schwertmann. 1974. Maghemite in soils and its origin. II. Maghemite syntheses at ambient temperature and pH 7. Clay Miner. 10:299–310.

Torrent, J. 1987. Rapid and slow phosphate sorption by Mediterranean soils: Effect of iron oxides. Soil Sci. Soc. Am. J. 51:78–82.

Torrent, J., and V. Barrón. 1993. Laboratory measurements of soil color: theory and practice. p. 21–33. *In* J.M. Bigham and E.J. Ciolkosz (ed.) Soil color. SSSA Spec. Publ. 31. SSSA, Madison, WI.

Torrent, J., and U. Schwertmann. 1987. Influence of hematite on the color of red beds. J. Sediment. Petrol. 57:682–686.

Torrent, J., U. Schwertmann, H. Fechter, and F. Alferez. 1983. Quantitative relationships between soil color and hematite content. Soil Sci. 136:354–358.

Van der Zee, S.E.A.T.M., M.M. Nederlof, W.H. Van Riemsdijk, and F.A.M. De Haan. 1988. Spatial variability of phosphate adsorption parameters. J. Environ. Qual. 17:682–688.

Wyszecki, G., and W.S. Stiles. 1982. Color science: Concepts and methods, quantitative data and formulae. John Wiley & Sons, New York.

Zeese, R., U. Schwertmann, G.F. Tietz, and U. Jux. 1994. Mineralogy and stratigraphy of three deep lateritic profiles of the Jos plateau (Central Nigeria). Catena 21:195–214.

Zhang, P., and D.L. Sparks. 1990. Kinetics of selenate and selenite adsorption/desorption at the goethite/water interface. Environ. Sci. Technol. 24:1848–1856.