The Effect of Pedogenic Environments on Iron Oxide Minerals

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I. Introduction

A. Role of Fe(III) Oxides* in Pedogenesis

Soil color is and has always been of interest to soil scientists around the world. It has entered into many classification systems and even modern classifications such as the US Soil Taxonomy use soil color at various levels.

Among the various colors, the hues between red and yellow are most widespread. They are caused by various forms and concentrations of Fe(III) oxides (Taylor, 1982; Torrent *et al.*, 1983). In a negative sense, the lack of Fe(III) oxides indicates the important pedogenic processes of Fe reduction and subsequent removal, thereby leaving the grey colors of the silicate matrix behind. Iron(II) compounds may induce green-blue or black colors.

These brief comments show that iron oxides can function as indicators of pedogenesis. Pedogenesis comprises the sum of all processes which have taken place in the soil mantle. These processes are induced by and are functions of a number of pedogenic factors (Jenny, 1980).

The primary reaction through which Fe(III) oxides are formed is the hydrolytic and oxidative decomposition of Fe(II)-containing primary minerals [mainly Fe(II) silicates]:

$$\underset{\text{Fe(II) silicate}}{\text{Fe(II)–O–Si}} + H_2O \xrightarrow{+O} \underset{\text{Fe(III) oxide}}{\text{–Fe(III)OH}} + \text{– SiOH} + e^- \quad [1]$$

The degree to which this irreversible reaction has taken place is useful for characterizing the degree of weathering. It varies widely between weakly and strongly developed soils and can be easily measured by the ratio of dithionite-soluble Fe to total Fe.

Once formed, Fe(III) oxides can be dissolved either through (microbial) reduction to Fe^{2+} or through complexation by organic ligands. Both, Fe^{2+} and Fe-organic complexes may again be the source for Fe(III) oxides through reoxidation (Eq. [2]) or hydrolytic decomposition (Eq. [3]), respectively:

$$Fe^{2+} + H_2O \xrightarrow{+O} -\text{Fe(III)OH} + H^+ + e^+ \quad [2]$$

$$\text{Fe(III)–O–C–R} + H_2O \rightarrow \text{–Fe(III)OH} + \text{HO–C–R} \quad [3]$$

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*For brevity this term will be used throughout this article as a group name for oxides and oxyhydroxides of Fe.

Just like every chemical reaction, all these Fe(III) oxide-forming reactions are governed by the reaction conditions which, in a pedogenic sense, are pedogenic factors.

In the above reactions Fe(III) oxides are considered as non-variable components. In reality this is not the case. So far, at least six different Fe(III) oxides have been identified in soils and although they are rather simple chemical compounds chemically—they consist only of Fe, O, and H—they differ considerably in their crystal structure and various other properties (Schwertmann & Taylor, 1977; Taylor, 1983). This fact is of great relevance to pedogenic research and is the basis for connecting the occurrence and association of certain Fe(III) oxides with those pedogenic factors which have led to their formation and in turn to the formation of a particular soil.

An essential requirement for the use of Fe oxides as pedogenic indicators is, of course, the ability to identify, quantify, and characterize the various mineralogical phases. Fortunately, methods to do so have been considerably refined in recent years. Among these are special X-ray diffraction techniques (Schulze, 1981), Mössbauer spectroscopy, high-resolution electron microscopy, and others, but simple chemical methods and even color estimation can also provide valuable information. For example, the concentration of hematite in various soils is correlated with the redness as measured by the Munsell notation (Torrent *et al.*, 1980) or, more accurately, by spectrophotometry (Torrent *et al.*, 1984) (Figure 1). This relation can, however, be different for different groups of soils.

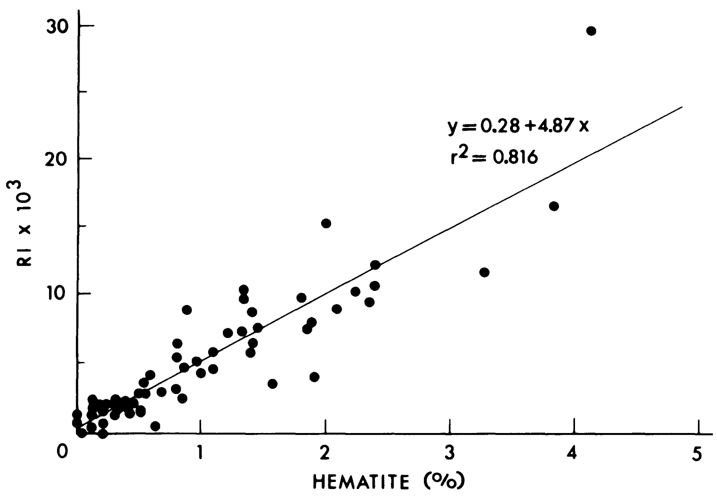


Figure 1. In B-horizons of various soils from Europe, the redness index was a linear function of percent hematite (from Torrent *et al.*, 1984).

B. Properties of Fe(III) Oxides

Properties of Fe(III) oxides which are particularly relevant to differentiation of the various *phases of Fe(III) oxides* are *color, solubility, thermal behavior*, and—most important—*structure*, which is the basis for all diffraction and spectographic methods of identification. For a tabulated summary of these properties see Schwertmann and Taylor (1977). In principle, the basic unit of the structure is the $Fe(O,OH)_6$ octahedron. The variation between phases is mainly due to a variation in the arrangement of these octahedra.

Crystal size and *morphology* are less typical for the different *pedogenic* Fe(III) oxides. They may well, however, reflect the variation of environmental conditions for a particular type of mineral. The same applies to what is generally known as *isomorphous substitution*, i.e. the replacement of iron in its octahedral position by other cations. So far, only substitution of Al for Fe has been shown to occur widely in soil Fe oxides. The extent of Al substitution reflects the activity of Al in the system which in turn is governed by pedogenic factors such as pH, type of Al compound, stability of Al-organic complexes, Si activity, etc.

This article will review the effect of various pedoenvironments on the mineralogical phases (section II), Al-substition (section III) and crystal quality (section IV) of Fe(III) oxides.

C. Ways to Study the Relation between Fe(III) Oxides and Pedoenvironments

Experimentally, there are two ways to study the relationship between Fe(III) oxides and pedoenvironments. *Firstly*, observations in the field may correlate the phases, properties, and quantity of Fe oxides with the pedogenic environments as described by such parameters as pH, base saturation, soil temperature, soil moisture, organic matter content, etc. *Secondly*, pedoenvironments may be simulated by *in vitro* experiments in which Fe oxides are synthesized under controlled conditions similar to those in soils. Because numerous parameters usually act together in soil environments, the *in vitro* experiments are often of limited value, but have produced interesting information in the past.

Once the environmental parameters, such as Fe activity, pH, activity of water, etc., are known in a particular soil or synthesis environment the question arises as to what extent the formation of the various Fe oxides can be predicted from thermodynamic data. Numerous stability field diagrams were constructed from these data and are in use. They usually show goethite to be the most stable Fe(III) oxide phase in most soil environments and goethite is indeed the most widespread Fe oxide mineral. However, very often goethite coexists with hematite where it would be expected to be the sole phase on the basis of its thermodynamic stability. Moreover, goethite is also frequently associated with other less stable phases such as lepidocrocite or ferrihydrite. It is obvious, therefore, that these systems are not in thermodynamic equilibrium, a situation which may last for pedogenetic time spans because the transformation of metastable phases into their stable counterparts may be kinetically hindered. This becomes plausible if one realizes that the transformation of one form into another occurs via solution and consists of a number of partial processes such as dissolution of the precursor, nucleation, and crystal growth of the end product. All of these may well be inhibited or at least drastically retarded in a highly "contaminated" system such as the soil.

In order to understand the relationship between environmental factors and the type of Fe oxide, the study of both the *mechanisms* and the *kinetics* of formation is equally necessary, as is the accurate determination of the therodynamic constants as a function of phase, crystal size, and isomorphous substitution.

II. Pedoenvironments and Fe(III) Oxide Minerals

The following will review the relationships observed so far between the various Fe oxides in soils and their pedogenic environments. Because only a few studies exist which attempt to correlate the occurrence of certain Fe oxides with measured environmental factors in the soil, these relations will be treated by the type of Fe oxides present rather than by environmental factors. Wherever possible these observations will be complemented by results from *in vitro* synthesis experiments.

A. The Goethite-Hematite Pair

As mentioned before, goethite (α-FeOOH) and hematite (α-Fe_2O_3) are the most widespread Fe oxides in soils. Their coexistence in many soils of the subtropical and tropical regions reflects their similar thermodynamic stability. Their relative proportions, however, cannot be readily explained by applying existing thermodynamic data. The postulation of Langmuir (1971, 1972) that goethite is unstable with regard to hematite if the crystal size is below 76 nm does not agree with the situation in many soils because most goethite crystals are in fact smaller (Taylor, 1984; Schwertmann & Kämpf, 1984). The higher stability of Al-substituted goethite over hematite, even if the former have smaller crystals than 76 nm (Nahon *et al.*, 1977; Yapp, 1983), cannot explain most situations either because many soil goethites have little or no Al substitution.

As deduced from numerous observations, important factors which influence the quantitative relationship between goethite and hematite are soil temperature, activity of soil water, soil pH, soil organic matter, and possibly also the release rate of Fe during weathering.

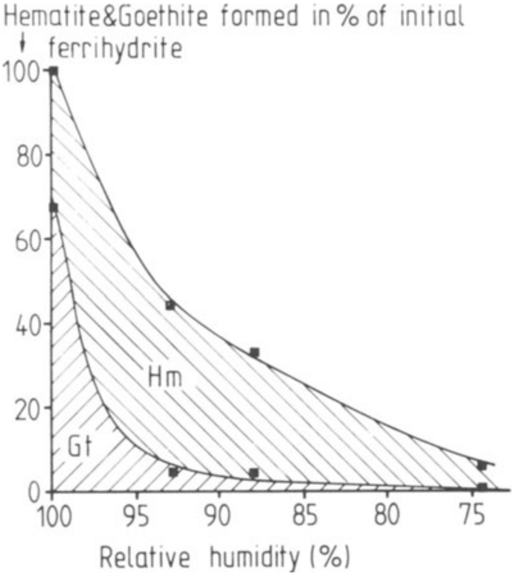


Figure 2. Effect of relative humidity (RH) on the crystalization of hematite (Hm) and goethite (Gt) from synthetic ferrihydrite at 45°C after 180 days. The shaded areas represent the average (4 samples) percentages of hematite and goethite formed with respect to the total crystalline products formed in liquid water (RH = 100). Adapted from Torrent *et al.* (1982).

1. Soil Temperature and Soil Water Activity

These two factors influence hematite formation through a dehydration process. This dehydration is, however, not the dehydration of goethite to yield hematite ($2\ \alpha\text{-FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O}$), as is often assumed, but is most likely the dehydration of ferrihydrite as a necessary precursor of hematite (Feitknecht and Michaelis, 1962; Schwertmann, 1966; Chukhrov *et al.*, 1973). Whereas goethite does not dehydrate to hematite at ambient conditions, ferrihydrite does, even in the presence of an excess of liquid water (Schwertmann, 1965).

All experiments in which ferrihydrite was converted to hematite and goethite have shown that hematite is favored as the temperature increases. These experiments were done at a water activity of 1 (presence of liquid water). In view of the fact that the water activity in soils of warmer regions may drop below 1, Torrent *et al.* (1982) investigated the effect of relative humidity (RH) on the crystallization of goethite and hematite from ferrihydrite at 45°C. They found (Figure 2) that with decreasing RH the rate of transformation decreased strongly, but also relatively more hematite was formed. At 28°C the rate of transformation was 50 times smaller than at 45°C. From these results it is believed that for hematite formation in soils, the variation in soil temperature may be more important than the variation in water activity.

The influence of temperature and moisture partly explains the zonal distribution of hematitic (reddish) and non-hematitic (goethitic yellowish-brown) soils. Cool humid areas are usually free of hematitic soils whereas in warmer areas reddish soils are widespread. Along climatic transects

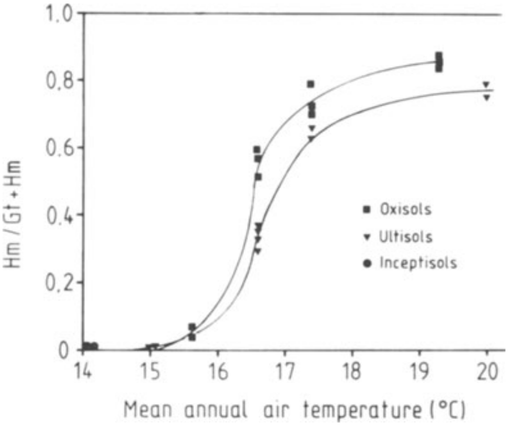


Figure 3. In soils of south Brazil the proportion of hematite (Hm) as against goethite (Gt) increased with increasing mean annual air temperature (From Kämpf and Schwertmann, 1982).

(*climosequences*) the hematite-goethite ratio of B-horizons has indeed been shown to increase with increasing air temperature and increasing water deficit as deduced from climatic data. Examples were presented for Ultisols and Inceptisols in South Brazil (Figure 3) (Kämpf and Schwertmann, 1982) and for Alfisols on Würmian glacial gravel in the Northern foreland of the Alps in Germany (Schwertmann *et al.*, 1982) (Figure 4).

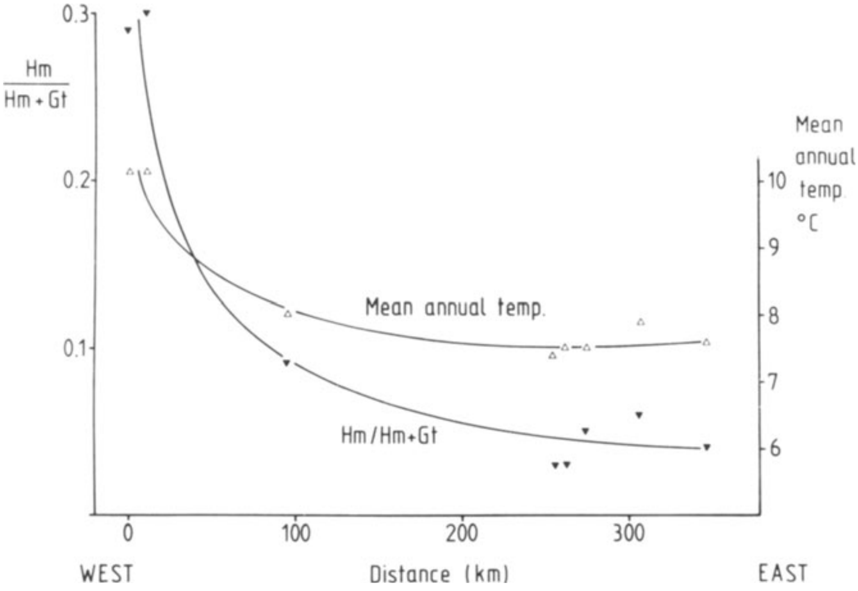


Figure 4. In the B_t horizons of Alfisols on Würmian calcareous gravel in south Germany the proportion of hematite (and the redness) increases as the mean annual temperature increases from 7.5°C in the east to 10.6°C in the west. (From Schwertmann *et al.*, 1982).

Temperature and moisture may also explain the variation in the hematite-goethite ratio in *toposequences* of soils: Taylor and Graley (1967) described a series of soils on basalt in Northern Tasmania, Australia, in which the reddish soils (3.75 YR) of the lower and drier coastal plain grade into yellow soils (7.5 YR) with increasing rainfall (1000 → 1500 mm) and decreasing temperature (12 → 9°C) as altitude increases from 0 to 600 m over a distance of 30–40 km. This was accompanied by an increase in the Gt/(Gt + Hm) ratio (Table 1) and is an example where the climate varies with altitude, with the soils varying accordingly.

On a smaller scale, Curi (1983) described a toposequence of soils weathered from basalt in Central Brazil. The entire sequence was only 176 m long and had an elevation difference of only 2 m. The Acrox profile on the drier upper slope position had a red (2.5 YR) B horizon with a Gt/(Gt + Hm) ratio of 0.19, while the yellow (10 YR) B horizon of the soil in the depressional position contained only goethite (Figure 5). In this example, pedoclimate variations are due to topography.

A similar example was reported recently from well-drained as against poorly drained Alfisols on Terraces of River Guadalquivir in Spain: All soils had goethite but hematite was only found in well-drained soils and some A horizons of the imperfectly drained soils (Pena & Torrent, 1984).

Red-yellow toposequences—although without hematite-goethite quantification—have also been described from other areas. In these cases the redness will prove that hematite is present and its concentration may be roughly estimated if the redness is quantified. In the highly dissected Coastal Plain of North Carolina, yellowish-brown Paleaquults prevail on the plateau, while redder Paleudults occur at the edge of the plateau where the water table is deeper and the soils are drier (Daniels *et al.*, 1975). Similarly, in Northern Queensland (Coventry *et al.*, 1983) Grey-, Yellow- and Red-Earths are topographically associated. A shallow lithic contact (shale) in the plateau soils causes a stagnant water regime and leads to yellow soils (even to grey soils where the reducing period is long). In contrast, on the lower slope

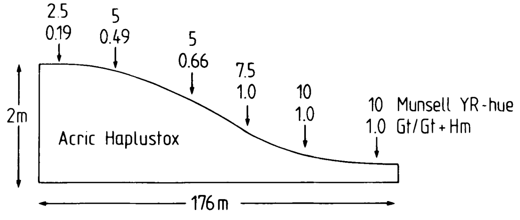
Table 1. Variation of the Goethite/Hematite ratio [Gt/(Gt + Hm)] in 11 profiles on Basalt of Northwest Tasmania with Temperature and Rainfall[a]

Altitude (m)	Average temp. (°C)	Annual rainfall (mm)	Organic matter[b] (%)	Average Munsell hue (YR)	Gt/Gt+Hm
0–175	12	1020–1140	5.6	3.75	0.58 ± 0.10
150–275	11	1140–1400	6.4	4.3	0.71 ± 0.06
275–450	10	1400–1780	6.8	6.0	0.75 ± 0.05
400–575	9	1520	7.8	7.5	0.74 ± 0.07

[a] Taylor and Graley, 1967.

[b] in A-horizons of one profile in each altitudinal zone (A.M. Graley, personal communication, 1983).

Figure 5. Color and goethite (Gt)-hematite (Hm) relations in Acrox profiles on basalt along a short toposequence in Central Brazil: Soils have less hematite and become yellower downslope. (From Curi, 1983).



position where the soils are highly permeable they are red. This again means that where the pedoenvironment is drier (and probably warmer) hematite is formed, whereas in the moist environment no hematite occurs. Unfortunately, this example from Queensland is the only one, where the associated water regime was also measured (Williams and Coventry, 1979). Studies in which soil temperature and soil moisture regimes are measured and directly related to the pedogenic Fe oxides would thus be very desirable.

2. Organic Matter

The dependence on soil climate makes it likely that organic matter (C) which itself is related to the soil climate may also influence the goethite/hematite formation in soils. Observations to this effect are similar to the ones of the preceding section:

(1) Soils of the cooler and moister climates, whether zonally or due to different altitudes, often have higher C-contents than those of warmer climates. The C-contents of A-horizons in typical profiles of the toposequence described in Table 5.1 decreased with decreasing altitude. In soils of Southern Brazil the Gt/(Gt + Hm) ratio increased with increasing organic C percentage (Figure 6).

(2) Soils which for topographic reasons (lower slope or depression) or for stratigraphic or pedogenic reasons have a moister water regime within the same climatic zone tend to have higher C-contents. Since both groups of soils tend to be more goethitic or even free of hematite it appears likely that a C-preserving pedoclimate favors goethite over hematite.

Three more observations support the "antihematitic" nature of an organic-rich environment:

(1) Root channels in reddish palaeosols often show a radial zonation of Fe distribution: A bleached zone immediately around the root is followed by a goethitic (yellow) zone free of hematite beyond which is the unaffected reddish bulk soil.

(2) In soils formed in a cool climate on hematitic parent materials such as red Mesozoic sandstones or from colluvial red soil material in

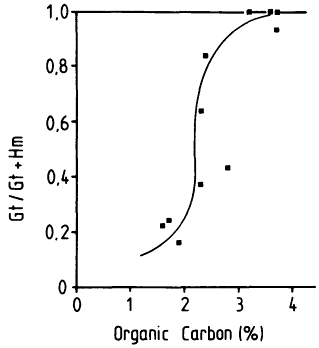


Figure 6. In the A-horizon of soils from south Brazil the proportion of goethite (Gt) relative to hematite (Hm) increased with increasing organic carbon (From Kämpf and Schwertmann, 1982).

depressions, the hematite is dissolved by reduction (or chelation) and upon reoxidation (hydrolysis) goethite, lepidocrocite, of ferrihydrite, but no hematite, is formed (Campbell & Schwertmann, 1984).

(3) In the tropics and subtropics soils which have a yellow A over a red B horizon are widespread. Here, again, the higher C-concentration in the A horizon may have prevented hematite from forming or may have led to a removal (Fey, 1983) or transformation (Schwertmann, 1971) of the former hematite to goethite.

The "anti-hematitic" effect of soil organic matter has not yet been explained satisfactorily. It appears insufficient to attribute it solely to a cool and moist pedoclimate which causes both a preferred formation of goethite and a high concentration of organic matter. Beyond this, a direct effect of organic substances may also be possible, as discussed in more detail elsewhere (Schwertmann *et al.*, 1984). In brief, organics may complex the Fe, thereby lowering the activity of inorganic Fe(III) ions in solution, which in turn prevents the solubility product of ferrihydrite ($\sim 10^{-37}$–10^{-39}), but not the much lower one of goethite ($\sim 10^{-42}$) from being exceeded. Because ferrihydrite is considered a necessary precursor of hematite this will logically prevent hematite formation and only goethite will be formed.

This hypothesis (Schwertmann, 1971) has not yet been verified experimentally. It seems in contradiction with the abundant formation of ferrihydrite in some environments of a cool humid climate (e.g. placic horizons, Campbell & Schwertmann, 1984). Ferrihydrite occurs where large amounts of Fe^{2+} are rapidly oxidized in the presence of compounds which inhibit the formation of crystalline FeOOH forms (silicate, organics, etc., Schwertmann *et al.*, 1984). However, due to the presence of these inhibitors the unstable ferrihydrite will slowly convert to goethite via solution but not to hematite.

3. Soil Acidity

The effect of pH in an Fe(III) system on the goethite formation from ferrihydrite was demonstrated by Knight and Sylva (1974) and more recently by Schwertmann & Murad (1983). They found that as the pH drops from 8 to

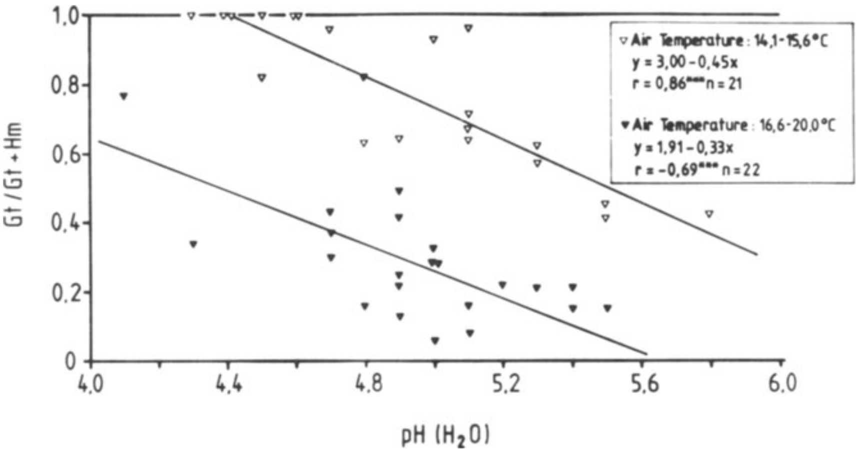


Figure 7. In soils of south Brazil the proportion of goethite relative to hematite increases with decreasing pH in the cooler eastern area whereas in the warmer western area this proportion appears to be more governed by other environmental factors such as soil temperature. (From Kämpf and Schwertmann, 1982).

4 the concentration of goethite increases relative to hematite parallel to the activity of the dominant monomeric $Fe(OH)_2^+$ species in this pH range. Obviously, this monomeric, monovalent species is the most suitable one for nucleation and growth of goethite crystals, i.e. for the goethite formation in solution. Whether or not this result is relevant to soil environments remains to be proven. A recent result of Kämpf and Schwertmann (1982) from 11 A-horizons of South Brazilian soils is in line with the *in vitro* experiment as seen from Figure 7: Within the pH range of 4–6 the proportion of goethite relative to hematite increased with decreasing pH, particularly if the climatic conditions were not too warm. In the warmer area the higher temperature which favors hematite seem to have the dominating effect.

4. Aluminum

Since there is more Al than Fe in many rocks, it will naturally be abundantly present in a soil environment where goethite and hematite form. Al may affect these two minerals in two ways: (1) it can enter the structure and replace Fe in its octrahedral position; (2) it may influence the goethite/hematite ratio. Both effects should be greater as the Al activity in solution increases, which in turn will be a function of the type of Al compound and the activity of their partners such as OH for Al hydroxides and silicate for Al silicates.

The effect of Al on the goethite/hematite ratio has so far been only demonstrated in various *in vitro* experiments. The results agree in so far as small amounts of Al strongly suppress goethite in favor of hematite formation

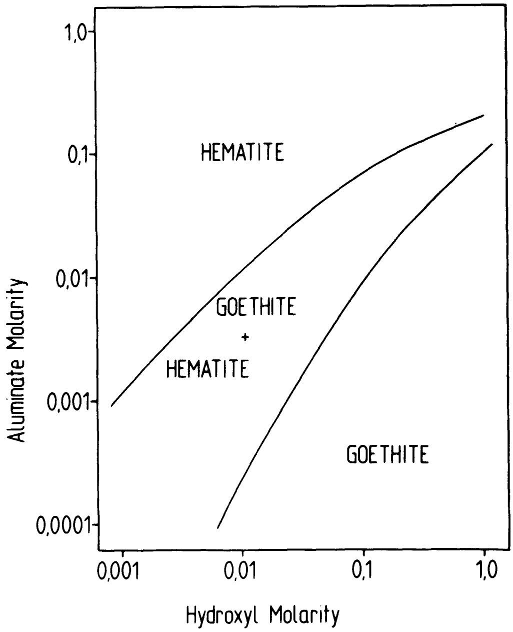


Figure 8. Increasing [OH] and decreasing [Al] in an alkaline system favors goethite over hematite during the transformation of ferrihydrite to these two minerals (From Lewis and Schwertmann, 1979).

from mixed Al-Fe(III) coprecipitates (Al-ferrihydrite) between room temperatures and 100°C (Callière *et al.*, 1960; Gastuche *et al.*, 1964; Wolska, 1976; Schwertmann *et al.*, 1979; Lewis & Schwertmann, 1979). The latter authors showed that at 70°C within an [OH] range of 10^{-3}–1.0 *M* and an [Al] range of 0–0.3 *M* the proportion of hematite increased with decreasing [OH] and increasing [Al] (Figure 8). At lower [OH], e.g. at pH 5–7, less than 1 mole % Al was found to be sufficient to completely supress goethite formation from these coprecipitates at 70°C (Schwertmann *et al.*, 1979).

At 25°C, although hematite is less favored than at 70°C, only 2.5 mole % Al was necessary to suppress goethite (Schulze, 1982). Experiments at ambient temperature are hampered by the strong retarding effect of Al on crystallization. Coprecipitates with $\geq$7.5 mole % Al were only less than half transformed into crystallaine oxides (hematite in this case) after more than 6 years whereas at 5 mole % and below complete transformation to goethite and hematite had taken place (Figure 9).

The relevance to soils of these results obtained at room temperature but in pure systems remains to be seen. Since highly Al-substituted goethite occurs abundantly in soils the hematite favoring effect of Al may be overshadowed by other factors, e.g. temperature, organic matter, and pH.

5. Conclusions

The process of hematite and goethite formation in the Fe(III) system and the factors influencing it as discussed in this chapter are summarized in

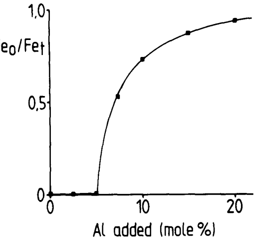


Figure 9. Effect of Al on the crystallization of hematite and goethite from mixed Al-Fe coprecipitates at 24°C after 3.28 yr. Degree of crystallization is measured by the ratio of oxalate (Fe_o) to total Fe (Fe_t) which is equivalent to the proportion of the precursor coprecipitate left. The graph shows that above a critical value of ~5 mole %, Al has a strong retarding effect on formation of goethite and hematite. (Schwertmann, unpubl.).

Figure 10. It can be seen that the various factors affect the formation during various stages of formation. High temperature and low moisture content may be more influential in the transformation of ferrihydrite to hematite because a dehydration step is involved during which the ferrihydrite loses its water and the Fe atoms must attain a consistent hematite structure. Soil temperature and moisture may, however, also affect the rate of Fe release from parent rocks with different Fe content and mineralogy. Basic igneous rocks may lead to soils higher in hematite than rocks with a lower Fe release rate as shown by yellow soils on shale next to red soils on dolerite dikes protruding through the shale in Natal, South Africa. Organic matter and pH, on the other hand, seem to be factors which also influence the concentration and form of inorganic Fe cations in the soil solution from which goethite and ferrihydrite (as a precursor of hematite) are formed. Furthermore, interrelations exist between soil temperature, soil moisture, and pH, on the one hand, and the C-regime, on the other hand. High temperature, good aeration, and neutral pH accelerate the turnover of organic matter in soils. Thus the goethite/hematite ratio is influenced by a network of pedoenvironmental factors.

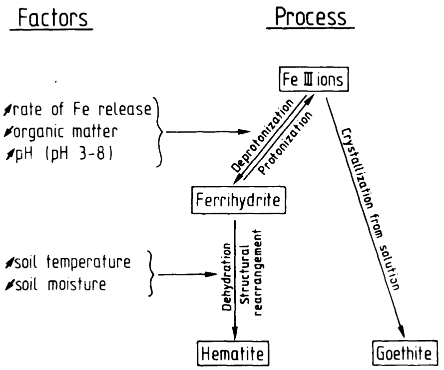


Figure 10. Hematite and goethite: Schematic representation of their competitive process of formation and factors influencing it. Small arrows indicate that increasing (↗) or decreasing (↘) expression of the factor favors hematite formation with opposite effect for goethite. One factor can affect two different processes: Higher soil temperature may not only induce dehydration of ferrihydrite and thereby reinforce hematite formation *directly* but may also accelerate Fe release and organic matter decomposition and thereby favor hematite formation *indirectly*.

B. Lepidocrocite

1. General Remarks

Lepidocrocite (γ-FeOOH) is metastable with regard to goethite ($\Delta G_f = -114$ kcal/mol as against -117 kcal/mol for goethite). However, if kinetically favored it will easily form in pedogenic environments and due to sluggish kinetics it may be stable even for pedogenic times. This can be deduced from its occurrence in many soils all over the world where it often can be recognized by its orange color (7.5 YR). It is frequently intimately associated with its polymorph goethite even within the same mottle, concretion, or pipestem. This creates the question of which factors may be responsible for the formation of either lepidocrocite or goethite in the same soil.

2. Presence of Fe(II)

Except for one occurrence (Ross and Wang, 1982), lepidocrocite in soils has exclusively been found in what are known as hydromorphic soils (Van der Marel, 1951; Brown, 1956; Schwertmann, 1959). In these soils O_2 deficiency temporarily occurs caused by an excess of water which fills most or all the pores, thereby limiting the amount of O_2 to the small concentration present in the pore water. When this O_2 is consumed by microorganisms during their metabolic oxidation of organic carbon, Fe(III) in oxides will take over the role of an electron acceptor and will be reduced to and mobilized as Fe(II). Fe(II) will then move to zones of higher redox potential where it will be reoxidized and new Fe(III) oxides will form.

These processes lead to a typical redistribution of Fe into Fe(III) oxide accumulations (mottles, concretions, etc.) and Fe(III) oxide-depleted zones and thus to soils with a typical morphology (reductomorphic soils) in which the Fe(III) oxides are distributed in a heterogeneous pattern as compared to a more homogeneous pattern in well-aerated soils.

Lepidocrocite is a typical mineral in these reductomorphic profiles and it can therefore be concluded that lepidocrocite needs Fe(II) as a necessary precursor. This is fully supported by synthesis experiments: oxidation of Fe(II) solutions at ambient conditions with pH controlled between 5 and 7 yields pure lepidocrocite of crystal morphology identical to soil lepidocrocite (Schwertmann, 1959, 1973), whereas lepidocrocite seldom forms from an Fe(III) system. The exact nature of the process of formation is not fully understood. Most likely greenish-blue Fe(II,III) hydroxysalts so-called *green rusts*, occur as intermediate phases (Taylor and McKenzie, 1980) but they must not necessarily be there.

In contrast to goethites, lepidocrocites in soils are usually reasonably well crystallized (corrected width at half-height of the (020) line at 6.27 Å is around 0.2–0.3°2Θ. Lepidocrocite of much lower crystallinity does form, however, if the rate of oxidation and thus the rate of crystallization is high. An example is shown in Figure 11. Orange mottles from *within* prismatic aggregates of a clayey pseudogley contained well crystallized lepidocrocite whereas lepidocrocite from neighboring pore walls was much less crystalline (and more reddish in color). A higher rate of Fe^{2+} supply and a faster oxidation are most likely to occur in the air-conducting coarse pores whereas within the aggregates the rate may be much lower.

Even lower crystallinities of lepidocrocites were found in ochreous deposits which form by rapid oxidation of Fe^{2+}-bearing waters as they appeared at the surface (Schwertmann and Taylor, 1979; Schwertmann and Kämpf, 1983). Thus crystal size of lepidocrocite may function as an indicator of rate of aeration in pedogenic environments although other factors such as pH (the lower the pH, the less well crystallized, Schwertmann and Thalmann, 1976) will also be of significance.

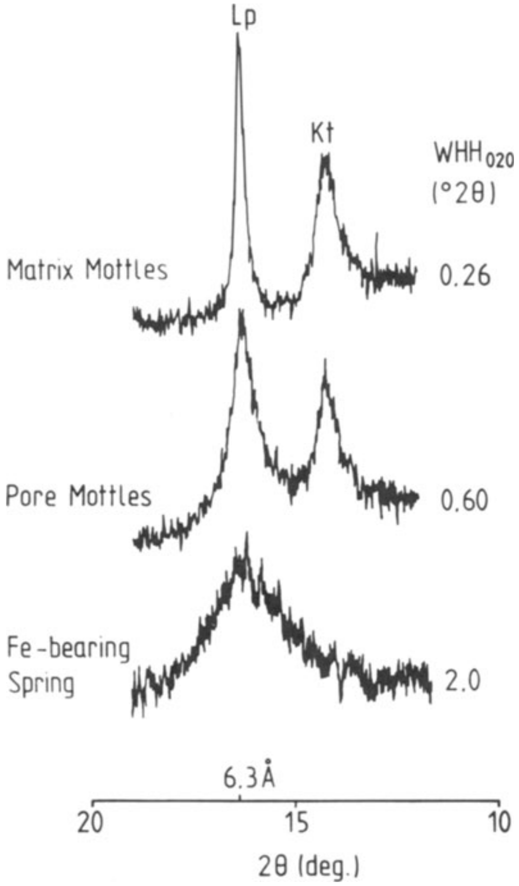


Figure 11. X-ray diffraction lines of lepidocrocites from various environments. The lepidocrocite found in mottles within aggregates of a reductomorphic clay soil is much more crystalline (i.e. has sharper XRD-lines) than the one found within large pores which in turn is more crystalline than a lepidocrocite from a Fe-bearing spring. (Schwertmann, unpubl.).

3. The Lepidocrocite-Goethite Pair

The intimate association of lepidocrocite with goethite in soils (but not with hematite) is considered the result of two competetive processes, with the reaction conditions determining which of the two minerals is favored. This concept is preferred over goethite formation *from* lepidocrocite because (1) the transformation of lepidocrocite to goethite under pedogenic conditions is very slow, and (2) because it is so easy to produce both in the same system at near-pedogenic conditions in *in vitro* experiments. Thus, the lepidocrocite–goethite pair appears to behave analogously to the hematite-goethite pair where two competitive processes are also responsible for their simultaneous formation.

An example for the close association of goethite and lepidocrocite was described in reductomorphic soils of Natal/South Africa (Schwertmann and Fitzpatrick, 1979). In pipestems, i.e. hollow, tubular Fe oxide accumulations around roots, the goethite concentration decreased as the pore was approached. Lepidocrocite and goethite intimately associated were also formed around rice roots within one season (Chen *et al.*, 1980).

The factors which govern the ratio of lepidocrocite to goethite in such environments are only partly known. Laboratory experiments may, however, help to explain the spatial distribution: When an Fe(II) solution is oxidized at room temperature and pH 7 with O_2 to which increasing concentrations of CO_2 are admixed, more and more goethite will from at the expense of lepidocrocite (which is the sole phase in the absence of CO_2) (Table 2). Since ample CO_2 may be produced by respiration or decomposition of the root in its immediate vicinity, goethite as opposed to lepidocrocite may be favored close to the root, thereby reflecting this specific microenvironment.

Table 2. Addition of Increasing Proportions of CO_2 to O_2 by Which a 0.05 *M* $FeCl_2$ solution is oxidized at pH 7, Room Temperature Resulting in Suppression of Lepidocrocite in Favor of Goethite[a]

CO_2 flow rate mL/min	Proportion (%) of lepidocrocite	goethite
0	100	0
0.014	100	0
1.74	100	0
3.0	35	65
4.7	3	97
14.4	0	100
30.8	0	100
56.5	0	100

[a] Schwertmann, 1959.

The lepidocrocite-suppressing effect of carbonate may also explain why lepidocrocite rarely occurs in calcareous soils (see also Blume, 1968) although one exception was reported recently (Ross and Wang, 1982). This general statement is not contradicted by recent experiments (Loeppert and Hosner, 1984) in which lepidocrocite formed from $FeCl_2$ solutions even in the presence of solid calcite. In these experiments the lepidocrocite was formed very quickly while the calcite reacted comparatively slow. Applying a higher P_{CO_2} to this system, less lepidocrocite was indeed formed. Therefore, lepidocrocite might well form in a soil where calcite is present because the large particles of calcite react very slowly. This underlines the important role of the reaction *rate* when pedogenic environments are simulated by laboratory experiments.

The mechanism behind the strong influence of carbonate ions on suppressing lepidocrocite is not yet known. If green rust is an intermediate phase then this phase will probably be in the carbonate form which appears more stable than the sulfate and chloride forms. The higher stability may then slow down the rate of its oxidation and transformation to FeOOH, and thus favor goethite over lepidocrocite.

Another factor which suppresses lepidocrocite and favors goethite in the Fe(II) system is aluminum. Again, this effect has only been demonstrated in laboratory synthesis at ambient conditions where >10 mole % Al completely suppressed lepidocrocite (Taylor and Schwertmann, 1978). In pedogenic environments this result may be relevant, because lepidocrocite appears less frequently in strongly acid soils even when they are reductomorphic (Blume, 1968).

4. Conclusions

Lepidocrocite commonly occurs as orange Fe oxide accumulations (mottles, pipestems, bands) in non-calcareous, clayey, reductomorphic (hydromorphic) soils of temperate climates. It is formed through oxidation of Fe^{2+}, and the rate of oxidation affects crystal size. Carbonate ions in the environment induce the formation of goethite which is often associated with lepidocrocite.

C. Ferrihydrite

1. General Remarks

Ferrihydrite is an only recently discovered Fe(III) oxide mineral of the bulk composition $5\ Fe_2O_3 \cdot 9\ H_2O$. Its structure has not been completely elucidated, but from X-ray and electron diffraction a defect hematite-like structure with vacant Fe sites and some replacement of O by H_2O has been proposed (Towe and Bradley, 1967; Chukhrov *et al.*, 1973; Schwertmann and Fischer, 1973). Because of its disordered structure, ferrihydrite has escaped identification by X-ray diffraction for a long time. Only recently have several occurrences in soils and other natural surface environments been described (Carlson and Schwertmann, 1981, 1984; Henmi *et al.*, 1980; Childs *et al.*, 1982; Murad, 1982; Schwertmann *et al.*, 1982; Campbell and Schwertmann, 1984). Also, the methods used to detect ferrihydrite in mixtures with other Fe oxides have been improved (Murad and Schwertmann, 1980; Schwertmann *et al.*, 1982). A simple extraction with acid oxalate (Fe_o) as compared to dithionite (Fe_d) gives a fair indication of the presence and amount of ferrihydrite.

Ferrihydrite occurs in nature either as the sole Fe oxide or in close association with goethite or lepidocrocite. Although it is considered a necessary precursor for hematite it has not been positively identified together with this mineral so far. The reason for this probably is that the transformation of ferrihydrite, once formed, to the much more stable hematite is much faster than the formation of ferrihydrite itself.

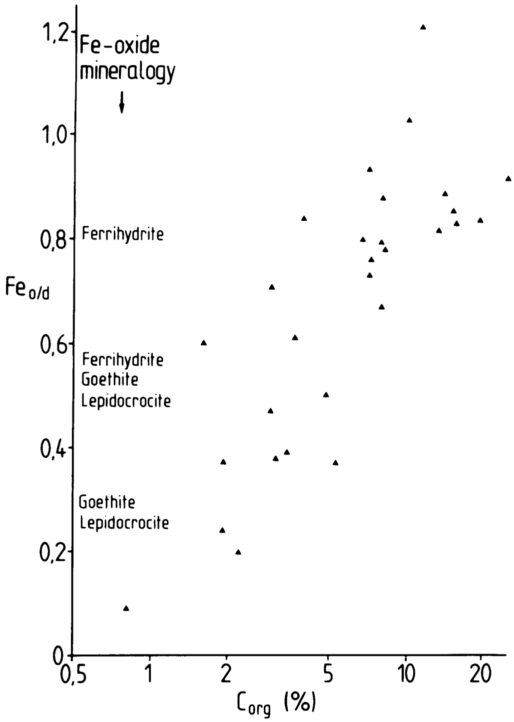
2. Pedogenic Factors

The high degree of disorder of ferrihydrite as compared to the other Fe oxides makes likely the assumption that either a rapid formation and/or hindrance of crystallization will cause the disorder. Both reasons are supported by the observation that ferrihydrite forms either when Fe^{2+}-containing waters are oxidized very quickly or—more importantly—in the presence of constituents which impede crystal nucleation and growth. Laboratory experiments have shown that such impedance can come from low concentration of organics, silicate, or phosphate and possibly from all those components which have a high affinity for Fe and which block the surface of the growing crystal.

The inhibiting effect of *organics* in soils was found to be strong in podsol B-horizons and placic horizons (Campbell and Schwertmann, 1984) and also in ochreous deposits from drainpipes or ditches (Süsser and Schwertmann, 1983). All of these materials had a high Fe_o/Fe_d ratio (>0.5), whereas in those samples where the organic matter was lower the Fe_o/Fe_d ratio was also lower and goethite and lepidocrocite were the dominant minerals (Figure 12). Ferrihydrite was also detected in lake waters containing approx. 1.5 mg/L of humics (Tipping *et al.*, 1981). In laboratory experiments it was found that among simple organic acids the carboxyl-hydroxyl acids such as citric acid are particularly strong inhibitors of crystallization (Schwertmann *et al.*, 1968; Cornell and Schwertmann, 1979; for a detailed review see Schwertmann *et al.*, 1984).

Another important constituent inhibiting crystallization and thereby favoring ferrihydrite over FeOOH is *silicate*. In Finland, Fe-containing ground waters are aerated for purification before being introduced into municipal water supply systems. On aeration, poorly crystalline ferrihydrite is precipitated which contains 2–6% Si strongly adsorbed at the ferrihydrite surface as indicated by IR bands at 930–960 cm^{-1} assigned to Si—O—Fe bonds (Carlson and Schwertmann, 1981, 1984). Ferrihydrite from Si-rich

Figure 12. In placic horizons the ratio Fe_o/Fe_d tend to increases with organic matter content. Accordingly, goethite and lepidocrocite are dominant at low Fe_o/Fe_d while ferrihydrite becomes dominant at high Fe_o/Fe_d. (From Campell and Schwertmann, 1984).



waters was also reported in New Zealand by Henmi *et al.* (1980) and by Childs *et al.*, (1982).

In simulation experiments, water with 20 mg Fe^{2+}/L was quickly oxidized by air, with and without soluble Si present (0–15 mg Si/L) (Schwertmann *et al.* 1984). A poorly crystalline lepidocrocite was formed at 0–4 mg Si/L whereas poorly crystalline ferrihydrite was the product at Si concentrations between 5 and 12 mg/L, thus proving the strong effect of Si on ferrihydrite formation. Further support for this concept comes from a study in which ochreous precipitates from stream water in a tropical area of Central Brazil turned out to consist of lepidocrocite and goethite rather than ferrihydrite (Schwertmann and Kämpf, 1983). Although Si concentration of the water was not measured it is likely to be low in this Oxisol-Ultisol landscape which has reached a high degree of desilification.

3. The Ferrihydrite-Goethite Pair

Bog iron ores (Schwertmann, 1959; Evans *et al.*, 1978), placic horizons (Campbell and Schwertmann, 1984), and lake ores (Carlson and Schwertmann, unpubl.) are natural Fe oxide accumulations consisting of various proportions of ferrihydrite and goethite. The XRD patterns of four typical examples are shown in Figure 13. The proportion of the two oxides can be roughly estimated from the Fe_o/Fe_d ratio which is also given in Figure 13. All of these formations are typical for humid temperate or cool climates in which organics are not rapidly decomposed (particularly under hydromorphic conditions) and/or the Si content of the Fe-bearing waters are reasonably high. As described before this would favor the formation of ferrihydrite. Whether the associated goethite has formed simultaneously or over time from the unstable ferrihydrite via solution is not yet known because no chronosequences have so far been studied.

4. Conclusion

In conclusion, ferrihydrite seems to be an indicator of pedogenic environments in cool or temperate, moist climates characterized by young Fe oxide formations and soil solutions relatively rich in compounds (organics, Si, etc.) hindering the immediate formation of goethite and lepidocrocite. The mineral therefore deserves attention wherever such situations occur and its presence can be detected by relatively high Fe_o/Fe_d ratios.

D. Maghemite

Maghemite is the cubic, ferrimagnetic form of Fe_2O_3 (γ-Fe_2O_3). It occurs frequently in subtropical and tropical soils (Taylor and Schwertmann, 1974; Fitzpatrick, 1978; Coventry *et al.*, 1983) but has occasionally been

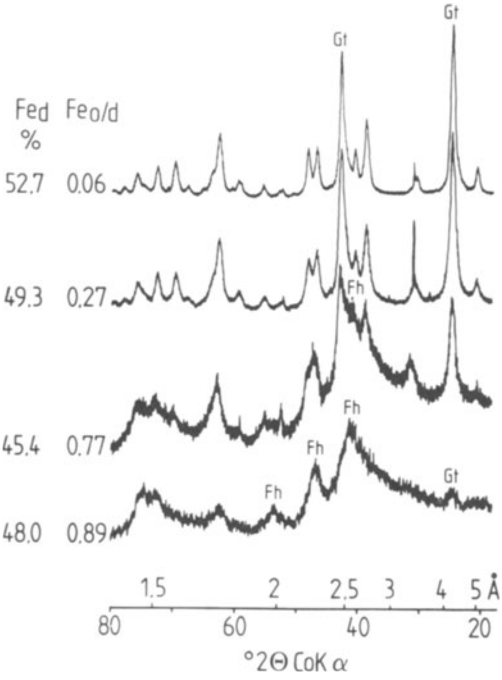


Figure 13. Ferrihydrite and goethite are often associated but, depending on crystallization conditions, their proportions may vary in a wide range as seen by these X-ray diffractograms and Fe_o/Fe_d ratios. The upper three samples are concretions from gleys and the lowest sample is an ochreous precipitate from a ferriferous spring.

identified in soils of the humid temperate area as well (Van der Marel, 1951; Schwertmann and Heinemann, 1959).

The pedoenvironment in which maghemite forms can be elucidated only if its formation is understood. Oxidation of magnetite is one realistic possibility, but it neither explains the occurrence of maghemite in soils whose parent rocks are very low in magnetite, nor its concentration near the surface. Another possibility is by oxidation of green rust at pH greater than 7 as shown in laboratory experiments (Taylor and Schwertmann, 1974; Taylor, 1980). Since green rust is limited to strong reducing conditions maghemite should only occur in reductomorphic soils and should also not be concentrated in the surface soil.

A third possibility is the transformation of any other pedogenic Fe oxide by heating to approximately 300–500°C in the presence of organic matter. This may happen during fires which frequently occur in subtropical and tropical areas. Where maghemite has been found in temperate regions, occurrences are limited to small areas containing charcoal and concentrated at the surface so that fire without doubt has caused its formation. A support for the postulate that fire caused the formation of maghemite also in warmer regions comes from the observation that these maghemites are Al-substituted (whereas magnetites as possible precursors are commonly not Al-substituted) and that Al-substituted goethites can easily be transformed into Al-substituted maghemites if heated to 450°C for 2 hr in the presence of sucrose (Schwertmann & Fechter, 1984). If this hypothesis proves right, then maghemite may indicate former fires in these areas.

In the tropics and subtropics maghemite seems to occur more in hematitic soils but not so much in goethitic soils. Moister environments in these areas such as at higher altitudes (Fitzpatrick, 1978) or local depressions (Curi, 1983) in which goethitic soils free of hematite prevail are also free of maghemite. It remains to be seen if this is so because under these conditions no maghemite is formed or, alternatively, maghemite is transformed to goethite as described for hematite (p. 180).

III. Aluminum Substitution

A. General Remarks

Because of its identical valency and its similar size ($r = 0.67$ Å for Al and 0.76 Å for Fe) the Al atom can replace Fe in its octahedral position in Fe(III) oxides. First discovered by Correns and von Engelhardt in 1943 in goethite and later described for soil goethites by Norrish and Taylor (1961) it is now established as a widespread phenomenon in soil iron oxides. Numerous studies of *synthetic* Al-substituted goethites and hematites have produced extensive knowledge about the influence of Al-substitution on the characteristics of these oxides (Schulze and Schwertmann, 1984; and references therein).

An important characteristic of Al-substituted Fe(III) oxides is their smaller unit cell size caused by the smaller size of Al. Schulze (1983) has found that the *c*-axis parameter of Al-goethites is linearly related to the degree of Al substitution and can therefore be used to quantify the substitution. This principle also applies to other Fe oxides and enables us to investigate the pedoenvironmental significance of Al substitution. The problem appears attractive because the Al substitution of soil goethites and hematites varies considerably depending on the type of soil in which the oxides were formed.

B. Goethite

The Al substitution of a large number of soil goethites was recently determined from different parts of the world: Natal/South Africa (Fitzpatrick and Schwertmann, 1982), south and central Brazil (Curi, 1983; Schwertmann and Kämpf, 1984a), West Africa (Nahon *et al.* 1977; Didier *et al.*, 1983) and Europe (Torrent *et al.*, 1984; Carlson and Schwertmann, unpubl.). The results are summarized in Table 5.3 where the samples are grouped according to their source and environment. It can be seen that the range of Al substitution in goethites lies between 0 and 33 mole %, i.e. maximally every third Fe atom may be replaced by Al. This upper limit agrees with synthesis studies (Thiel, 1963; Schulze, 1983).

The following conclusions can be drawn from the data in Table 3: Low substitution prevails in weakly acid soils and in hydromorphic environments, while substitution above 10 or 15 mole % is usually found in goethites from

Table 3. Al Substitution Range of Goethites from Various Sources

Sample group	Area	No. of samples	Al subst. (mole %)	Reference[a]
Lake iron ores	Finland	16	<3	1
Bog iron ores	F.R.G.	10	<3	1
Concretions in hydromorphic soils	Mid-Europe	10	<3	1
Hydromorphic soils	South Africa	44	0–10	2
Ferricretes	South Africa	37	2–15	2
Alfisols, mod. acid	South Africa	7	7–12	2
Placic horizons	Europe	14	4–13	3
Bauxites, saprolites	South Africa	32	10–28	2
Ultisols, Inceptisols	South Brazil	47	11–25	4
Ultisols	South Africa	36	15–31	2
Oxisols	Central Brazil	12	24–36	4,5

[a] 1: unpublished 2: Fitzpatrick and Schwertmann, 1982; 3: Campbell and Schwertmann, 1984; 4: Schwertmann and Kämpf, 1984; 5: Curi, 1983.

highly weathered soils of subtropical and tropical areas. Particularly in Oxisols, goethites have often reached their maximum capacity of substitution.

No *in vitro* experiments have been conducted to explain these differences. In goethites prepared under alkaline condition the substitution is usually <20 mole % and a linear function of the Al concentration in solution (Lewis and Schwertmann, 1979). In goethites formed by oxidation of $FeCl_2$-$AlCl_3$ solutions under neutral conditions Al-substitution reaches 33% (Fey and Dixon, 1981: Goodman and Lewis, 1981; Schulze, 1983). How these results can help to explain the variation of Al substitution in soil goethites is not yet clear. The higher substitution in goethites from acid soils may well reflect the higher solution activity of Al as pH decreases. However, since most of these soils, particularly Oxisols, are not extremely acid it is more likely that the low Si concentration in these soils which causes a high Al activity is the reason for the high degree of Al substitution (Didier *et al.*, 1983). Correspondingly, goethites of weakly desilicified soils such as the younger soils in temperate areas, even if acid, are of low Al substitution. Besides being a function of Al activity in solution the substitution may also depend on the Al content of precursor phases such as green rusts which can be aluminous (Taylor and MacKenzie, 1980).

In hydromorphic soil goethites form from Fe^{2+} which is oxidized in larger pores where O_2 is available. Solutions in larger pores are further away from solid Al sources which supply Al for substitution, leading to low substitution.

C. Hematite and Other Fe(III) Oxides

Aluminum substitution of soil hematites has not been studied as systematically as that of goethites. So far, no hematites have been found with more than *ca.* 15 mole % Al (Nahon *et al.*, 1977), i.e., half the maximum substitution of goethites, again in agreement with synthesis experiments (Schwertmann *et al.*, 1979). Accordingly, where goethite and hematite occur in the same sample their Al substitution is in around a 2:1 ratio (Schwertmann and Kämpf, 1984a). This suggests that the Al substitution of hematite does not provide any additional information on the pedoenvironment if that of coexisting goethite is known.

Al-substituted *lepidocrocites* have not been found in soils, except in one soil on the island of Tonga (C. Childs, personal communication). Synthesis experiments have shown that small amounts of Al in an Fe(II) system suppress lepidocrocite in favor of goethite (Taylor and Schwertmann, 1978; Schwertmann, unpubl.).

Soil *maghemites* indicate measurable Al substitution by their reduced cell size and by extractable Al (Schwertmann and Fechter, 1984). It is suggested that these maghemites have formed from Al-substituted goethites at high temperatures caused by fires, a process which can easily be simulated in the laboratory. Al-substituted maghemites would then indicate the occurrence of fires in the past.

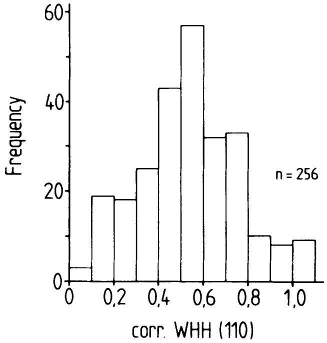
IV. Pedoenvironments and Crystal Quality

Because no specific results are available on this topic only a few observations will be discussed. *Goethite* and *hematite* crystals from soils often do not show the well-expressed morphology which is characteristic of synthetic preparations. Particularly poorly formed goethite crystals were observed in goethite accumulations of C-rich environments such as bog iron ores (Schwertmann and Taylor, 1977; Schwertmann and Schieck, 1980) whereas goethites in saprolites may have somewhat more distinct crystal shapes (Schwertmann and Kämpf, 1984). In most soils goethite and hematite form very small (10–30 nm) subrounded crystals, often strongly aggregated into microaggregates rather than associated with clay mineral surfaces (Jones *et al.*, 1982; Kämpf, 1981; Schwertmann and Kämpf, 1984). In contrast to goethite and hematite, better-formed crystals exist for soil *lepidocrocites*. Laths with serrated ends on two opposite sides occur in orange mottles of reductomorphic soils which are very similar to those produced *in vitro* under similar conditions (Schwertmann, 1973).

Low crystallinity of Fe oxides in soils obviously reflects the pedoenvironment. Numerous laboratory experiments have suggested a mechanism: several compounds frequently present in the soil solution strongly interfere with crystal growth. This applies particularly to those which have a stronger affinity for the Fe oxide surface such as organics, silicate, and phosphate, but also for aluminum (see earlier chapters). The presence of these compounds on the surface of natural Fe oxides, such as silicate on the ferrihydrite surface (Schwertmann and Fechter, 1983) proves this point. It is therefore essential that in studying the behavior of Fe(III) oxides in soils using pure synthetic minerals as model substances, the model minerals should resemble natural ones as much as possible to make the results meaningful for soils (Schwertmann and Taylor, 1981).

From these observations it appears useful to characterize Fe oxides by their crystallinity (crystal order and size) in addition to their identification and Al substitution to gain a further pedoenvironmental characteristic. A simple index for crystallinity is the width of the X-ray lines. As shown in Figure 14 goethites from very different soil environments indeed show a wide range of line widths. This indicates that the conditions for crystal development can vary considerably between different soil environments. In addition, differential line broadening may give some information about the crystal development in different crystallographic axes. Soil hematites often show broad (*hkl*) but sharp (*hk*0) lines indicating better crystal development in the crystallographic x-direction (plate width) than in the z-direction (plate thickness) (Schwertmann *et al.*, 1977). Since crystallinity reflects crystal size (see Schwertmann and Kämpf, 1984 for geothites) it should also be an

Figure 14. 265 soil goethites show a wide variation in crystallinity as measured by the width of their (110) X-ray diffraction line. (From Schwertmann and Kämpf, 1984).



important characteristic of Fe(III) oxides with regard to their ability to retain phosphate and other solution compounds.

V. Iron Oxide Minerals and Soil Classification

The nature and amount of Fe oxides have entered soil classification and nomenclature systems worldwide either directly or indirectly. Soil names which refer to brown or red colors are numerous in all languages and refer indirectly to the absence of hematite (only goethite = yellow-brown) or presence of hematite (= red) without explicitly naming these minerals. When efforts to quantify soil properties for classification were intensified in recent years, it was mostly the total or some fractional amounts of Fe oxides which were used, rather than the minerals themselves. This is the case, for example, for the Spodosols but also for two of the mineralogical classes, viz. "ferritic" and "oxidic."

A proposal to use the goethite/hematite ratio was recently made for Ultisols and Oxisols of South Brazil (Kämpf and Schwertmann, 1982) which were all dominated by kaolinite (kaolinitic class) and differed only in their goethite/hematite ratio. A tentative limit was set at a goethite/goethite + hematite ratio of 0.6 to differentiate between a kaolinitic-goethitic (>0.6) and a kaolinitic-hematitic (<0.6) class. This limit roughly corresponds to a moist Munsell hue of 6.25 YR and an air dry hue of 3.75 YR. Curi (1983) proposed the use of the hematite/goethite association for Oxisols in Central Brazil through the Munsell hue even at the Great Group level, defining Rhodorthox by a hue redder than 5 YR (hematite dominates) and Haplorthox by a hue less red than 5 YR (goethite dominates).

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