

## ION EXCHANGE

The interchange of ions of like charge between a solid and an aqueous solution in contact with it. In cation exchange the ions are positively charged, in anion exchange they are negatively charged.

### Bibliography

Sposito, G., 1989. *The Chemistry of Soils* (Chaps. 8 and 9). New York: Oxford University Press, 277 pp.

### Cross-references

Adsorption  
Exchange Phenomena  
Soil Chemistry  
Soil Fertility  
Soil Mineralogy

## IONIC ACTIVITIES

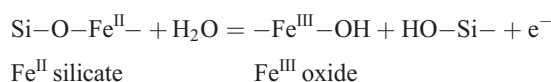
See *Soil solution*.

## IRON OXIDES

### Basic reactions

With 5.1 mass-%, iron is the fourth most abundant element of the Earth's crust. It exists predominantly in the divalent state and is located in silicates such as pyroxene, amphibole, biotite and olivine as well as in sulfides (e.g., pyrite, FeS<sub>2</sub>).

Once exposed to aerobic weathering, Fe<sup>2+</sup> will be readily oxidized to Fe<sup>3+</sup> which, in the common pH range of soils, will immediately hydrolyze and form sparingly soluble Fe<sup>III</sup> oxides (in the following used as a group term embracing all compounds in the system Fe–O–H). The overall weathering reaction is schematically represented by:



The electron e<sup>-</sup> is transferred to oxygen (O<sub>2</sub> + 4e<sup>-</sup> = 2O<sup>2-</sup>), readily available in aerobic soils. The proportion of the Fe in the parent rock "weathered" into Fe<sup>III</sup> oxides through this reaction can be taken as one measure of the degree of weathering. It ranges between a few percent for young to almost 100% for highly matured soils.

Once formed, the sparingly soluble Fe<sup>III</sup> oxides can not be redissolved by the reversal of hydrolysis (protonation), but complexation (mainly with organic ligands) or, more importantly, biotic reduction may bring about redissolution. Biotic reduction takes place in those parts of a soil where biological metabolism of biomass causes O<sub>2</sub> deficiency i.e., at a redox potential (Eh) of <0.1 V. In this case, immobile Fe<sup>3+</sup> in oxides is reduced to mobile Fe<sup>2+</sup> ions by electrons from the oxidation of biomass (represented by CH<sub>2</sub>O):



Thus, one C supplies 4 electrons to reduce four Fe<sup>3+</sup>. The corollary is that Fe<sup>III</sup> oxides are an important oxidant of organic matter (including xenobiotics) if oxygen is lacking. Conditions for microbial reduction in a soil are water saturation and the presence of metabolizable organic matter, e.g., biomass. The Fe<sup>2+</sup>, once mobilized, may migrate in the profile, eventually being reoxidized on reaching a zone of higher Eh. New Fe<sup>III</sup> oxides are then formed. The reoxidation is usually abiotic except at very low pH (e.g., in acid sulfate soils and in ARD) where the kinetic hindrance is surmounted by specific bacteria, e.g., *Thiobacillus ferrooxidans*. This redox process occurs repeatedly during pedogenesis and leads to or turns a homogeneous into a heterogeneous distribution of Fe<sup>III</sup> oxides in so-called redoximorphic soils, thereby reflecting the mosaic of aeration, visually expressed as differential staining. It is also responsible for the redistribution of Fe in whole landscapes in almost any climatic region. Local concentrations vary in shape and hardness. Spherical forms can be soft (e.g., mot-tles), or hard (e.g., nodules, glauco-bules and concretions). Hardening of a complete horizon produces the commonly very hard accumulations of Fe<sup>III</sup> oxide called ferricrete.

### Iron oxide minerals of soil

The intensive yellow, brown and red colors of Fe<sup>III</sup> oxides make their nature and spatial distribution in soils easily recognizable, and these colors often form the basis for naming (Red Earth, Terra rossa, Brunizem etc.) and classifying soils. The color variations are caused by different Fe oxide minerals in the system Fe–O–OH (or Fe<sub>2</sub>O<sub>3</sub>–H<sub>2</sub>O). The mineralogical, physical and chemical characteristics of those oxides, which are repeatedly found in soils – and only these are treated here – are listed in Table I2.

Minerals are defined by their crystal structure and by their chemical composition. Only a brief description of the structure is given here. The Fe-oxides consist of layers of the (large) O and OH ions which are either hexagonally close packed (hcp), as in goethite and hematite, or cubically closed packed (ccp), as in lepidocrocite and maghemite. The small Fe<sup>III</sup> cations (*r* = 0.067 nm) occupy the interstices between the O anions (*r* = 0.14 nm), thus forming an octahedron having as immediate neighbors either 6O i.e., –[FeO<sub>6</sub>]– as in hematite, or 3O and 3OH i.e., –[FeO<sub>3</sub>(OH)<sub>3</sub>]– as in goethite (Figure I32). In addition, –[FeO<sub>4</sub>]– tetrahedra with four O neighbors occur e.g., in magnetite and maghemite. Thus, the Fe may be either 6- or 4-coordinated with O (<sup>v</sup>Fe or <sup>iv</sup>Fe). The octa-dra may be connected to each other via faces, edges or corners leading to different Fe–O bond lengths. In the OH-containing forms the octahedra arrays are bridged by H-bonds.

The Fe<sup>III</sup> in the octahedral position may be partially replaced by other trivalent metal cations of similar size, such as Al<sup>III</sup>, Mn<sup>III</sup>, Cr<sup>III</sup> and V<sup>III</sup>, but divalent metals (Ni, Co, Cu, Zn, Ti) may also be incorporated. This is called *isomorphous* substitution, because the structure itself is not modified. It leads to partial solid solutions, which are common in soils between goethite (named after the famous German poet), α-FeOOH, and dias-pore, α-AlOOH, and between hematite, α-Fe<sub>2</sub>O<sub>3</sub>, and corundum, α-Al<sub>2</sub>O<sub>3</sub>, which have the same structure. Substitution modifies the properties of the Fe-oxides such as unit cell size, spectrographic behavior, magnetic properties, color, solubility and dissolution kinetics.

**Table 12** General physical and chemical characteristics of iron-oxide minerals occurring in soils (see Cornell and Schwertmann, 2003)

Mineral name: Formula:	Hematite $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Maghemite $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	Magnetite Fe <sub>3</sub> O <sub>4</sub>	Goethite $\alpha$ -FeOOH	Lepidocrocite $\gamma$ -FeOOH	Ferrihydrite (6-line) Fe <sub>1.55</sub> O <sub>1.66</sub> (OH) <sub>1.34</sub>
Crystal system	Trigonal	Cubic or tetragonal	Cubic	Orthorhombic	Orthorhombic	Hexagonal
Cell dimensions (nm)	$a = 0.50340$	$a = 0.834$	$a = 0.839$	$a = 0.388$ $b = 0.9956$ $c = 0.30215$	$a = 0.4608$ $b = 1.254$ $c = 0.307$	$a = 0.296$
Usual crystal shape	$c = 1.3752$ Hexagonal plates Rhombohedra	$c = 2.5014$ Cubes	Cubes	Needles, laths	Laths, needles	Spheres
Density (g cm <sup>-3</sup> )	5.26	4.87	5.18	4.26	4.09	3.96
Color	Red	Reddish-brown	Black	Yellow-brown	Orange	Red-brown
Solubility product <sup>§§</sup> (pFe + 3 pOH)	42.2–43.3	40.5	43.4–44.0	40–44	~42	38–39.5
Most intense XRD Spacings (nm)	0.269, 0.251 0.366	0.251, 0.295 0.147	0.253, 0.297 0.1485	0.418, 0.245 0.269	0.626, 0.329 0.247	0.250, 0.221 0.196, 0.148
Type of magnetism*	<i>wfm</i> or <i>efm</i>	<i>fim</i>	<i>fim</i>	<i>afm</i>	<i>afm</i>	<i>sp</i>
Neel (Curie) temperature (K)	956	(820–986)	(850)	400	77	25–115 <sup>#</sup>

<sup>#</sup>Blocking temperature.\**wfm*: weakly ferromagnetic; *afm*: antiferromagnetic; *fim*: ferrimagnetic; *sp*: speromagnetic.<sup>§</sup>Changes with substitution for Fe by cations for different radii.<sup>§§</sup>Depends on particle size.

The various Fe oxide minerals differ mainly in the arrangement of the octahedra in space (Figure I32). The FeOOH forms consist of double bands of edge-sharing FeO<sub>3</sub>(OH)<sub>3</sub> octahedra running along the crystallographic *b*-direction in goethite and the *c*-direction in lepidocrocite. In *goethite*, the double bands are linked by corner-sharing oxygens forming 2 × 1 octahedral arrangements and hydrogen bonds run across the bands. In *lepidocrocite* the double bands of octahedra share edges to form zig-zag layers which are connected by hydrogen bonds. In *schwertmannite* four double chains of octahedra form a 2 × 2 tunnel in which sulfate anions are supposed to be located. In all these FeOOH minerals only half of the octahedral interstices are occupied by Fe<sup>III</sup>. *Hematite* consists of layers of FeO<sub>6</sub>-octahedra, which are linked by edge- and face-sharing, and are stacked parallel to the *c*-direction. Two-thirds of the octahedral interstices are filled with Fe<sup>III</sup>. Some distortion of the octahedra, and the absence of H bonds, yield a more compact structure than the FeOOH form. This is responsible for the high density (5.26 g cm<sup>-3</sup>) of the mineral.

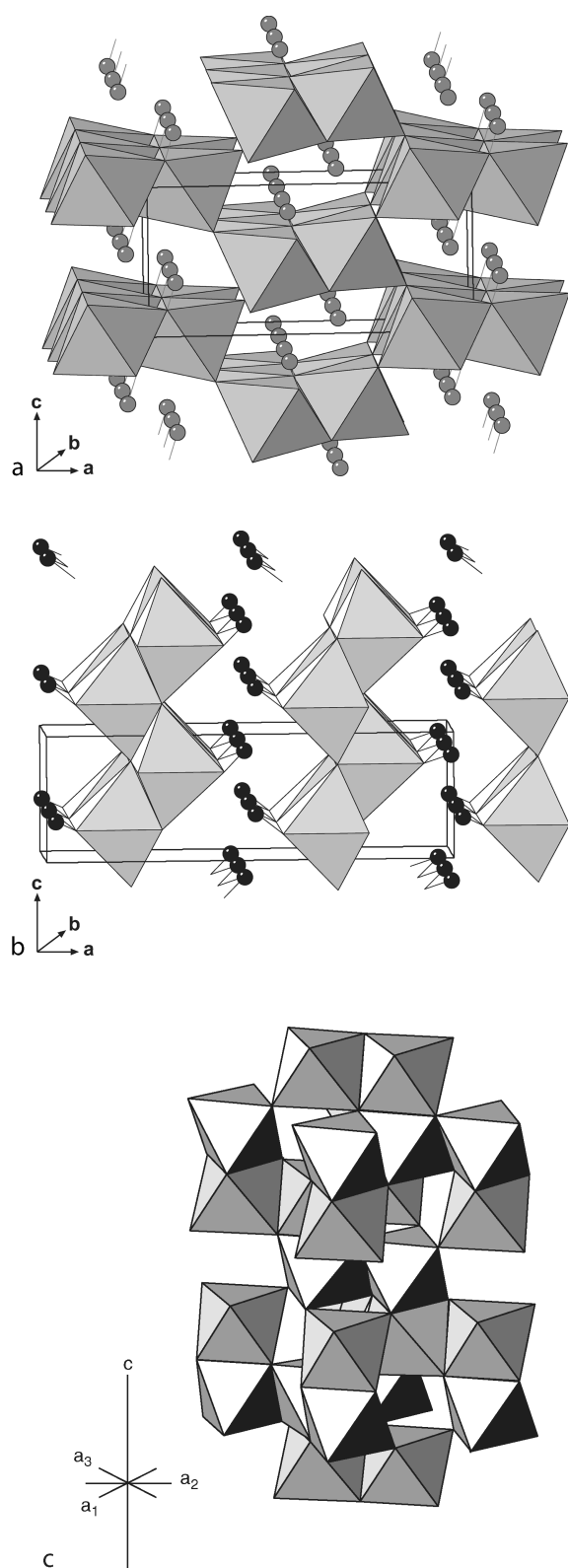
The crystallinity of ferrihydrite may vary considerably, as evidenced by the number (between 2 and 6–7) of broad X-ray diffraction peaks, which are used to further differentiate them. After Drits et al. (1993) the best ordered form (6-line) contains three intergrown structural components: (1) a defect-free one consisting of ABACA... anion close packing with the Fe-atoms (50% occupancy) only at octahedral sites, and a hexagonal unit cell with  $a = 0.296$  nm and  $c = 0.949$  nm and a space group P-31c; (2) a defective one with ABA and ACA structural fragments occurring with equal probability in a random sequence and with the Fe-atoms within each fragment being identically ordered in a hexagonal super-cell with  $a = 0.5126$  nm, space group P3, and (3) about 25% ultradispersed 1–2 nm hematite. A general formula is Fe<sub>5</sub>O<sub>5</sub>(OH). The main difference between 6- and 2-line ferrihydrite is in the size of their crystal domains. The formula for synthetic 6L sample Fe<sub>1.55</sub>O<sub>1.66</sub>(OH)<sub>1.34</sub> and Fe<sub>1.42</sub>O<sub>1.26</sub>(OH)<sub>1.74</sub> for synthetic 2L ferrihydrite.

*Magnetite* and *maghemite* differ from the foregoing Fe-oxides by having two types of metal-O-arrangements in their cubic structures: 1/3 of the Fe is Fe<sup>IV</sup> and 2/3 is Fe<sup>VI</sup>. In magnetite all

metal sites are filled with Fe with the tetrahedral positions being completely occupied by Fe<sup>3+</sup>, while the octahedral sites contain equal amounts of Fe<sup>3+</sup> and Fe<sup>2+</sup>. This results in a unit cell formula of <sup>iv</sup>Fe<sub>8</sub><sup>3+</sup><sup>vi</sup>(Fe<sub>8</sub><sup>3+</sup>Fe<sub>8</sub><sup>2+</sup>)O<sub>32</sub>. In maghemite only 5/6 (21<sup>1</sup>/<sub>3</sub> instead of 24) of the total available metal sites are filled by Fe<sup>3+</sup>; the remaining sites being vacant. The vacancies may be ordered tetragonally to give superstructure XRD peaks and the formula is Fe<sub>2.67</sub>?<sub>0.33</sub>O<sub>4</sub>, where ? signifies vacancy. *Limonite* and *hydrated ferric oxide* (HFO) are obsolete mineral names.

### Properties of soil Fe<sup>III</sup> oxides

1. They are strong pigments and give many soils their red, yellow, orange or brown color even at low concentrations (a few percent). The mineral-specific color results from their interaction with visible light and depends on both the crystal structure and particle size. It can be characterized by reflectance spectra in the visible range, by chromaticity parameters or simply by the Munsell color notation (hue, chroma, value).
2. They occur as minute crystals, often poorly ordered, ranging between about 5 and 100 nm in size. The crystal shape may be characteristic of a specific oxide (see Table 12) but equant, poorly defined particles often occur. Due to the small size, the oxides have a very large specific surface area between about 50 and 300 m<sup>2</sup> g<sup>-1</sup> and contribute substantially to the surface area of soils even at low concentrations.
3. Their surface is covered with OH ions attached to Fe<sup>III</sup> atoms. These are called surface functional groups and contribute substantially to the specific adsorption of various anions as inner sphere complexes. Common sorbates are phosphate, silicate, arsenate and humic compounds, as well as cations such as heavy metals. This adsorption makes the soil mantle act as an efficient sink for these ions and molecules thereby restricting their mobility in terrestrial ecosystems.
4. They have a very low solubility (pFe<sup>3+</sup> + 3pOH = 38–44; Table 12) so that free Fe<sup>3+</sup> ions only occur in extremely acid soils. The solubility increases with decreasing crystal size. It also increases if reduction to Fe<sup>2+</sup> occurs (i.e., at Eh << 0.1 V), and if ligands forming strong Fe complexes are present (e.g., citrate, humics).



**Figure I32** Idealized structural models of goethite (a), lepidocrocite (b) and hematite (c). The small circles indicate hydrogen bonds (H. Stanjek, unpubl.).

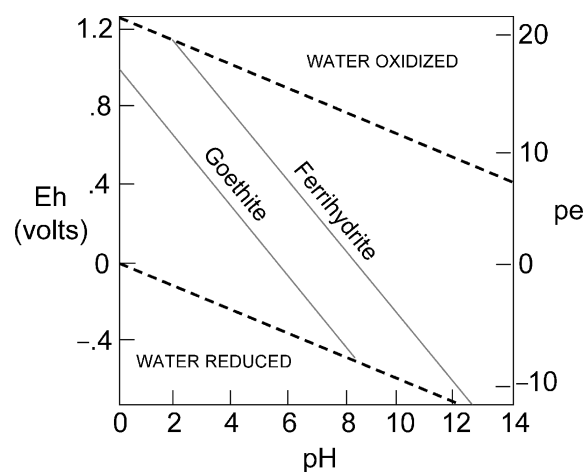
5. With respect to *isomorphous substitution* (see above), Al-for-Fe substitution is very common in soils. Up to  $\frac{1}{3}$  of the Fe positions in goethite and up to  $\frac{1}{6}$  in hematite may be occupied by Al. This substitution stabilizes the Fe-oxides, as shown by a decrease in the rate of dissolution by protonation and by reduction.
6. Due to their poor crystallinity (small crystal size and structural disorder), unspecific particle shape and low concentration in soils, their *identification* (e.g., by X-ray diffraction) is often difficult and requires Fe-specific methods, such as Mössbauer spectroscopy.

### Occurrence and formation

All Fe oxide minerals listed in Table I2 have been identified in soils or similar earth-surface environments and can be readily synthesized in the laboratory under ambient conditions. The close link between the occurrence of Fe<sup>III</sup> oxides and their mechanism of formation facilitates correlating their presence with pedogenetic conditions. This has been shown by a survey of Fe<sup>III</sup> oxides in various soils around the world.

*Goethite* and *hematite* are by far the most common Fe-oxides in soils. This is partly due to their high thermodynamic stability (see Table I2). The much higher stability (lower solubility) of goethite relative to ferrihydrite is shown by the Eh–pH diagram in Figure I33 (see also below). At a given pH, goethite produces the same Fe concentration in solution, as ferrihydrite only at a much lower Eh. Lepidocrocite is intermediate in stability. However, in spite of their lower stability, metastable forms such as lepidocrocite and ferrihydrite often occur in soils, particularly in younger soils characterizing the non-equilibrium state in the pedoenvironment. This is because the formation of these oxides is kinetically favored and their transformation to the stable forms is kinetically hindered, e.g., by an association with adsorbed ions or molecules, such as phosphate and organics. Nonetheless, the Fe-oxides of older soils, e.g., ultisols and oxisols, are mostly goethite or goethite and hematite.

With respect to their global distribution, soils of the subtropics and tropics often contain hematite in addition to goethite, in widely varying ratios and are therefore red, whereas soils in temperate regions are usually free of hematite and are dominated by goethite, which makes them yellow-brown. In view of



**Figure I33** Eh–pH relation for goethite and ferrihydrite at a Fe<sup>2+</sup> activity of  $10^{-4}$  M l<sup>-1</sup> and at 100 kPa and 25 °C.

their similar thermodynamic stability, it is essential to understand their mechanisms of formation in order to interpret the widely varying ratios of these two oxides. To this effect, numerous synthesis experiments have been conducted to simulate goethite and hematite formation under soil conditions, and their results may be very briefly summarized as follows:

Goethite either forms through slow oxidation of  $\text{Fe}^{\text{II}}$  ions or solid  $\text{Fe}^{\text{II}}$  compounds such as pyrite or siderite or, alternatively from ferrihydrite. When ferrihydrite is the precursor, goethite formation competes with that of hematite (Figure I34), which, in contrast to goethite, needs ferrihydrite as a precursor. Whereas goethite forms *via solution* from dissolved, partly

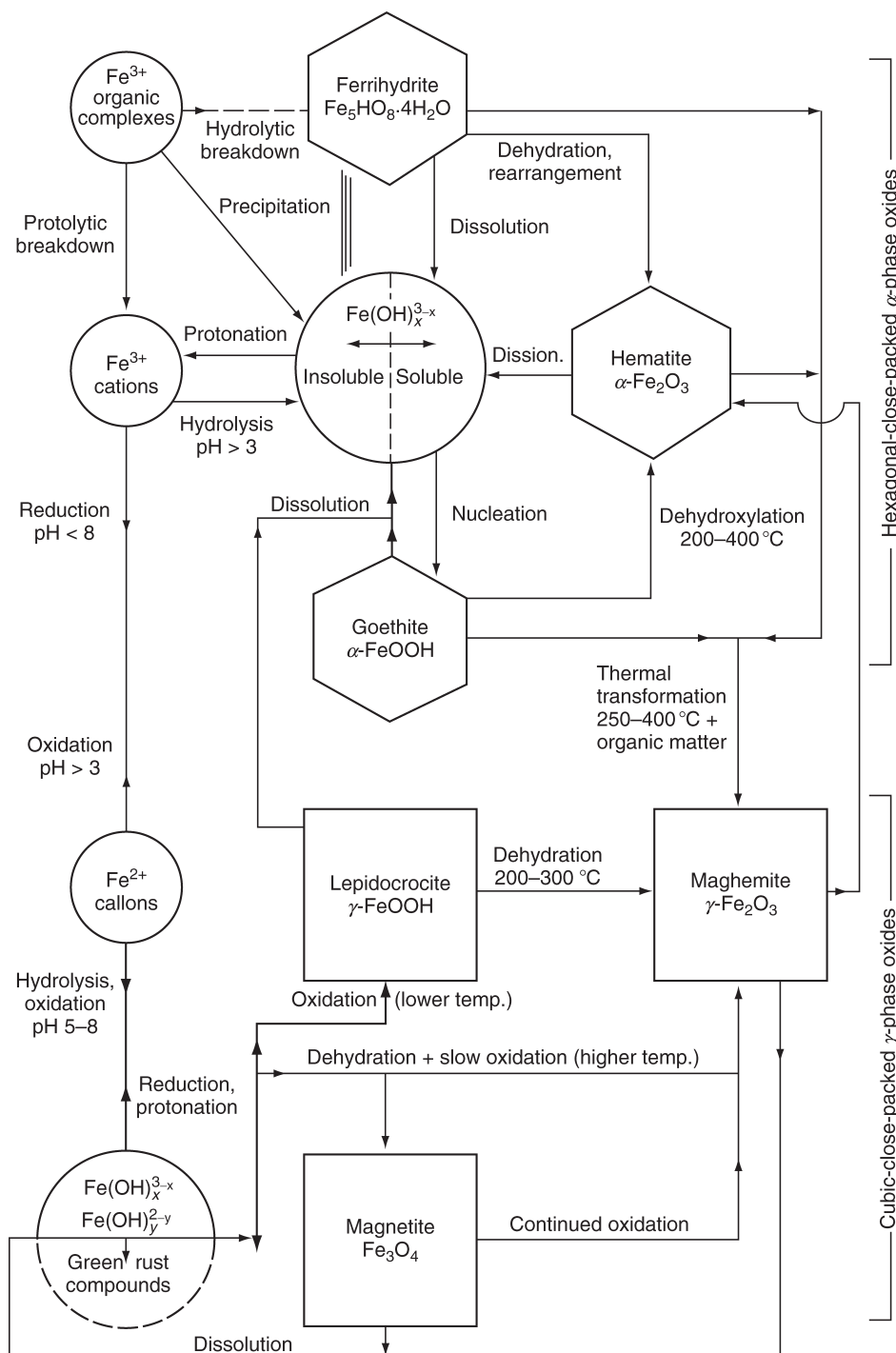


Figure I34 Common pathways of iron oxide formation and transformation.



hydrolyzed  $\text{Fe}^{\text{III}}$  ions (e.g.,  $\text{Fe}(\text{OH})_2^+$ ) by nucleation and crystal growth, hematite crystals are believed to nucleate and grow within the nano-sized ferrihydrite aggregates.

Numerous factors direct these two competing processes in one or other direction, leading to widely varying ratios of the two oxides in soils. Among these factors are temperature (shown for the range of 4 to 30 °C), water activity, pH and Al-concentration. Hematite is favored over goethite in warmer and drier pedoclimates because these promote dehydration over dissolution of the ferrihydrite. Furthermore, conditions favoring ferrihydrite formation may also favor the formation of hematite. Among the former are fast Fe release from Fe minerals and rapid turnover of organic matter, thereby, avoiding Fe-organic matter complexes. In soils a direct transformation of goethite to hematite by solid-phase dehydration is unlikely because the temperature needed is usually too low. Nor has "rehydration" of hematite to goethite been observed. Admittedly, the coexistence of ferrihydrite and hematite in soils has not been found so far.

Besides the global distribution, regular variations in the goethite/hematite ratio in soil sequences (pedosequences) can also be observed on smaller scales. Usually, more hematite relative to goethite is formed as the regional climate becomes warmer and drier. Examples of such climosequences are found with an east-west orientation over several hundred km in southern Brazil and in southern Germany, and also as a function of altitude in Lebanon and Tasmania. Hematite-goethite ratios also vary along topo(hydro-)sequences over several hundred or thousand meters, where the soils in drier up-slope positions have more hematite than those in moister depressions. For a similar reason red soils (terra rossa) on hard limestone, rich in hematite, are closely associated in Mediterranean regions with rendzinas low in hematite on soft, marly limestone. At a profile scale, yellow topsoils are often found over red subsoils. The absence of hematite in these topsoils has been ascribed to the presence of labile organic matter, which has either inhibited hematite formation, or microbial oxidation (iron respiration) has caused the preferential reductive dissolution of originally formed hematite – turning red soils yellow (xanthization). At an even smaller scale, Fe oxide mottles or concretions can have goethitic rims and hematitic interiors.

*Lepidocrocite* forms in soils through the oxidation of dissolved  $\text{Fe}^{2+}$  directly or via a green rust intermediate (Figure I34). If, however, the concentration of carbonate ions ( $\text{HCO}_3^-$  over most of the pH range for soils) in solution is substantial, as in calcareous soils or around respiring roots, goethite rather than lepidocrocite will be the oxidation product. Lepidocrocite, therefore, frequently occurs in non-calcareous redoximorphic soils of various climates where  $\text{Fe}^{2+}$  is formed by biotic reduction (see above). It occurs as mottles, bands or pipe stems and can be recognized by its orange color (5–7.5YR). *Schwertmannite* forms only in so-called acid-sulfate soils, i.e., in the presence of high concentrations of sulfate and at very low pH.

*Ferrihydrite* occurs, commonly with goethite, in soils of temperate and cool climates, especially in concretions, oxidation horizons of gleyed soils (e.g., bog iron ores), Podzol B horizons and in drains and ditches of lowland soils. It usually forms when  $\text{Fe}^{2+}$ -containing soil water is aerated relatively quickly, or occurs in the presence of compounds with a high affinity for the Fe oxide surface, for example organic matter, phosphate and silicate, which inhibit the formation of the better crystalline  $\text{FeOOH}$  forms. Under these conditions proper structural order is not achieved. Furthermore, the above adsorbates

will block or retard the transformation of ferrihydrite to the more stable goethite. On the other hand, ferrihydrite may be easily redissolved by reduction if, because of a rising water table, oxygen becomes deficient. In any case, given enough time, ferrihydrite can be expected to transform to a more stable Fe oxide and so is generally considered to be a relatively young Fe oxide.

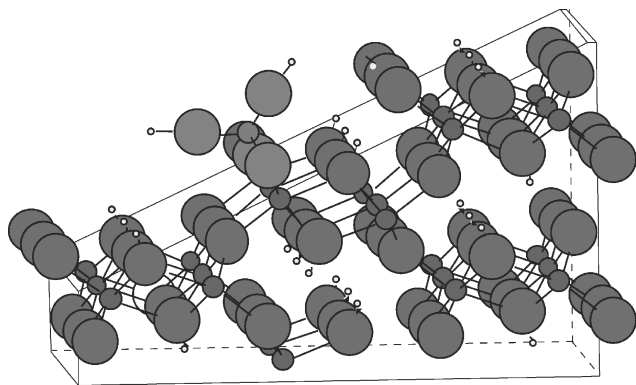
*Magnetite* in soils is usually inherited from rocks. Recently, however, pedogenic magnetite has been reported. It is most likely of bacterial origin, similar to the magnetite of so-called magnetotactic bacteria. Bacterial magnetite in so-called magnetosomes probably results from the intracellular reaction of ferrihydrite with dissolved  $\text{Fe}^{2+}$  as simulated in synthesis experiments at ambient temperature and neutral pH. Magnetite can oxidize to *maghemite* or to hematite. The solid-state transformation to maghemite requires a migration of Fe within the structure and an addition of O atoms to change from  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$ . The widespread occurrence of maghemite in soils of the tropics and subtropics (from which it can be readily separated by hand magnet) is associated with heat caused by open fires. At 300–400 °C, a temperature easily reached during bush fires, goethite and other Fe-oxides are converted into maghemite, particularly under restricted  $\text{O}_2$  supply. Essential in this process is the presence of organic matter as a reductant during the dehydration of the precursor oxide. The association of maghemite with corundum ( $\text{Al}_2\text{O}_3$ ) in soils proves the participation of fire.

### Significance of Fe-oxides in soil

Besides their pedological significance, Fe-oxides strongly affect a number of soil properties, which will only be briefly mentioned here. Among these are color (Table I2), surface adsorption of numerous ions and molecules, soil aggregation, and redox behavior.

*Surface adsorption* operates through Fe–OH groups at the surface of Fe-oxides and results from the completion of the ligand shell of surface Fe atoms. These groups attain negative or positive charge by dissociation ( $\equiv\text{FeOH} \rightarrow \equiv\text{FeO}^- + \text{H}^+$ ) or association ( $\equiv\text{FeOH} + \text{H}^+ \rightarrow \equiv\text{FeOH}_2^+$ ) of protons, depending on the pH of the surrounding solution. The pH at which the surface concentrations of  $\equiv\text{FeOH}_2^+$  and  $\equiv\text{FeO}^-$  groups are equal, the so-called point of zero charge, is generally around pH 8–9 for all Fe-oxides. The magnitude of the pH dependent charge is proportional to  $(\text{pH} - \text{pH}_{\text{pzc}})$  and to the ionic strength of the equilibrium solution. The charge will be in the range of several  $\mu\text{mol}$  per  $\text{m}^2$  of oxide surface.

The Fe–OH groups form surface complexes with a range of cations, especially heavy metal-hydroxy cations ( $\text{MOH}^+$ ), and oxyanions such as phosphate, silicate, arsenate and chromate. The surface OH groups can have one, two or three Fe atoms as nearest neighbors. These singly, doubly and triply coordinated OH groups exhibit different reactivities (acid strength) with the singly coordinated group being by far the most reactive one. The association is by chemical bonds via O- or OH-bridges and is called specific adsorption, or an inner-sphere complex. Although pH-dependent, it takes place even if the net surface charge has the same sign as that of the adsorbate. Phosphate adsorption by Fe-oxides is of great ecological importance and has been widely studied. It reacts with two singly coordinated Fe–OH groups to form binuclear, bidentate  $(\text{Fe}-\text{O})_2-\text{PO}_2\text{H}$  complexes (Figure I35). With goethite, the (110) face is usually the main crystal face and carries one singly coordinated OH per unit cell surface area. This would amount to a binding capacity

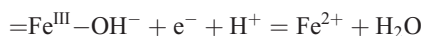


**Figure I35** A phosphate molecule forming a bidentate, binuclear complex with two single coordinated surface Fe atoms on the (110) surface of a goethite crystal.

of about  $2.5 \mu\text{mol P m}^{-2}$  of surface, a value which has been found for synthetic and natural goethites from soils and other surface environments. Among the toxic ions, arsenate and chromate have a high affinity for Fe-oxide surfaces, as have humic substances.

**Aggregation and cementation.** A contribution of Fe-oxides to soil aggregation and cementation is usually assumed but has not been accepted unequivocally. Aggregation into microaggregates ( $<1 \text{ mm}$ ) is particularly obvious in oxisols and ultisols rich in goethite and hematite. Cementation by Fe-oxides exists in concretions and ferricretes where Fe-oxides fill part of the pore space in which their crystals grew. Removal of Fe-oxides by dithionite often leads to complete dispersion. Addition of synthetic Fe-oxides, especially those with high surface area such as ferrihydrite, has aggregated soils or soil components. Microscopic and microprobe observations have demonstrated both intimate association with, as well as separation of, Fe-oxides from other soil materials, such as kaolinite. Complete or partial dispersion of microaggregates by organic anions (oxalate, citrate), however, was also achieved although only a small proportion of their Fe-oxides were extracted. These anions may have caused dispersion by modifying the surface charge of the Fe-oxides.

**Redox behavior.** All soils have the ability to buffer electrons produced preferentially during the metabolic oxidation of biomass by microorganisms.  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  bound in oxides, are important electron acceptors in anaerobic soils and can prevent methane formation under anoxic conditions. Electron titration of soils have shown buffer ranges corresponding to the thermodynamic stability of various  $\text{Fe}^{\text{III}}$  oxides according to the general reaction:



which consumes protons.

The  $(\text{Fe}^{2+})/(\text{Fe}^{3+})$  activity ratio in soils is controlled by the redox potential  $E_h$ , which may also be expressed as electron activity:

$$(\text{e}^-) = 10^{E_h/0.059} \text{ at } 25^\circ\text{C}$$

or by its negative logarithm  $p_e$ , which is analogous to pH.

According to the Nernst Equation:

$$E_h = E^\circ + 0.059 \log a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}$$

where  $E^\circ$  = standard potential, and  $a_{\text{Fe}^{3+}}$  and  $a_{\text{Fe}^{2+}}$  are the ion-activities.

In the presence of  $\text{Fe}^{\text{III}}$  oxides,  $a_{\text{Fe}^{3+}}$  is controlled by the solubility product of the specific  $\text{Fe}^{\text{III}}$  oxide and can be incorporated into  $E^\circ$ , leading to

$$E_h = E^\circ - 0.059 \log a_{\text{Fe}^{2+}} - 0.177\text{pH}$$

As seen from this equation, the  $\text{Fe}^{2+}$  activity increases as  $E_h$  and pH decrease. Using common thermodynamic data,  $E^\circ$  (in volts) may be taken as 0.73, 0.71, 0.86 and 1.06 for hematite, goethite, lepidocrocite, and ferrihydrite, respectively. With these values, the curves shown in Figure I37 were computed for  $\text{Fe}^{2+}$  activity of  $10^{-4} \text{ mol l}^{-1}$  (approximately  $6 \text{ mg Fe}^{2+} \text{ l}^{-1}$ ). The diagram shows that this  $\text{Fe}^{2+}$  activity will be reached at a pH and  $E_h$  which are higher the more soluble the  $\text{Fe}^{\text{III}}$  oxide, i.e., in the order ferrihydrite  $>$  lepidocrocite  $>$  hematite  $\approx$  goethite. In other words, along this line the oxides become less reducible. For goethite and hematite the reducibility also decreases with increasing Al-for-Fe substitution. In soils, however, the  $\text{Fe}^{2+}$  concentration may be limited by the solubility of sparingly soluble  $\text{Fe}^{\text{II}}$  phases, such as magnetite  $\text{Fe}_3\text{O}_4$ , vivianite  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , siderite  $\text{FeCO}_3$  and  $\text{Fe}^{\text{II}}$  sulfides, if the solubility products of these phases are exceeded. Furthermore,  $\text{Fe}^{\text{II}}$ -humic complexes may form. In this way, the formation of soluble  $\text{Fe}^{\text{II}}$ -organic complexes may lead to an increase in total  $\text{Fe}^{2+}$  concentration, and thereby foster the reductive dissolution of  $\text{Fe}^{\text{III}}$  oxides.

A considerable variety of bacteria can reduce  $\text{Fe}^{3+}$  from  $\text{Fe}^{\text{III}}$  oxides to meet their Fe requirement (dissimilatory  $\text{Fe}^{\text{III}}$  reduction). The detailed mechanism of electron transfer is not yet fully understood. An immediate contact between the bacterial cell and the  $\text{Fe}^{\text{III}}$  oxide particle speeds up the reaction, indicating that the electron is located at the surface of the cell. In addition, humic acid may function as an electron shuttle between the electron donor (metabolized organics) and the electron accepting  $\text{Fe}^{\text{III}}$  oxide. The rate of bacterial reduction was found to increase in the order goethite, hematite  $<$  lepidocrocite  $<$  ferrihydrite. The difference in rates between the different oxides was, however, more a function of their surface area than of their solubilities.

### Determination

The total amount of  $\text{Fe}^{\text{III}}$  oxides in soils is usually determined by an extraction with the strongly reducing Na-dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) in a buffered solution ( $\text{Fe}_d$ ). Other reducing agents of different strengths (e.g., ascorbic acid, hydroxylamine,  $\text{TiCl}_3$ ) are also used. Acid oxalate (pH 3) extracts poorly crystalline  $\text{Fe}^{\text{III}}$  oxides ( $\text{Fe}_o$ ), especially ferrihydrite, as well as organically-bound Fe and fine-grained magnetite. The ratio  $\text{Fe}_o/\text{Fe}_d$  is frequently used to characterize the degree to which Fe-oxides have transformed to goethite and hematite, because the latter two are barely soluble in oxalate solution. In acid soils rich in organic carbon, such as spodosols, pyrophosphate is used to extract organically-bound Fe, though some ferrihydrite is also extracted (by dispersion).

To identify and quantify various Fe oxide minerals, non-destructive methods must be used. This is often hampered by their low concentration of a few percent. Therefore, concentration procedures, such as particle size separation and preferential dissolution of kaolinite and gibbsite by boiling 5 M NaOH, facilitate the determination. X-ray diffraction is still the most widespread method for identification and quantification. In some cases, its potential is improved when used in a differential fashion. A Fe specific and very useful non-destructive method is Mössbauer spectroscopy ( $\gamma$ -ray absorption spectroscopy).

Also used are infrared and Raman spectroscopy, thermal analysis and magnetometry.

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## Cross-references

Aggregate Stability to Drying and Wetting  
 Aggregation  
 Mineral Analysis (Geochemistry Volume)  
 Soil Color  
 Soil Mineralogy  
 Sorption Phenomena  
 Weathering Systems in Soil Science

## IRON PAN

See *Pan*.

## IRRIGATION

### Objectives and constraints

The primary objective of irrigation is to supplement natural rainfall that may be insufficient in amount or temporal distribution in order to obtain high, stable yields in an intensive

cropping system. Secondary objectives may include modification of microclimate for frost protection or crop cooling, facilitation of germination and emergence by moistening the surface soil, leaching of salts from the root zone, incorporation of fertilizers and other chemicals, and disposal of sewage effluent. Different irrigation methods vary in their ability to meet these objectives.

In order to maintain land productivity, assuring both high and stable yields, irrigation practice must meet certain constraints – a well-known problem recently included under the term “sustainability”. Problems commonly encountered are physical damage to fields by erosion, silting of reservoirs and water courses, pollutant transport to ground or surface waters, deterioration of soil structure due to inappropriate or untimely tillage operations or poor water quality, crusting due to rain-drop or sprinkler drop impact, water logging and salinization of soil due to seepage from canals and over-irrigation. Once these problems make their appearance, the financial and social costs of the required land reclamation by far outweigh the cost of timely prevention.

Today water can be applied to a field on the one hand by techniques collectively known as *surface*, *gravity* or *flood irrigation*, and on the other hand by *pressurized delivery*. In the context of this entry these terms will refer to the actual method used to spread water on the land, and not necessarily for describing how water is conveyed to the field. Irrigation is almost as old as civilization itself, having started 5 000, and perhaps as early as 7 000 years ago in the ancient Near East (Gulhati and Smith, 1967; Marr, 1967). However, pressurized water application became possible only with the development of engine-powered pumps during the Industrial Revolution of the 19th century. Because of the limitation of human or animal power to pumping small discharges and low lifts (Molenaar, 1956), large scale irrigation first developed on flat, low lying valley lands adjacent to rivers, from which water could be diverted, conveyed and spread over the land by gravity. Valley soils are usually also the most fertile soils available. For most of its long history, irrigation has therefore been synonymous with gravity or surface irrigation. Along with the above advantages, valley soils have the disadvantage of intrinsic vulnerability to land degradation processes. Because of their location in the landscape, valley lands are often underlain by a fairly shallow water table, which may rise rapidly into the crop root zone due to over-irrigation, causing water-logging of the soil. Since most soils and watersources in arid and semi-arid regions contain some soluble salts, and water that evaporates from the soil surface or from crops is chemically pure water, the salts are left behind in the root zone and unless there is adequate rainfall and natural drainage, eventually reach concentrations harmful to crop growth. This accumulation can be prevented or corrected by leaching the salts downward out of the root zone by application of water in excess of evapotranspiration, which is tantamount to controlled over-irrigation. However, the leachate can only be removed by causing it to flow to a sink at a lower elevation, i.e., by drainage. Thus drainage water will invariably be more saline than the irrigation water. If artificial drainage is required, this is at best a costly operation. At worst, in the case of lowland valley soils the gradient may be insufficient to remove the drainage water, making drainage impossible without pumping.

There is evidence that some of the ancient civilizations in the Middle East underwent several cycles of prosperity and decline, accompanied by parallel fluctuations in the state of



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