NATURAL OCCURRENCE OF FEROXYHITE (δ'-FeOOH)

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Abstract—Feroxyhite (δ'-FeOOH) in association with goethite and lepidocrocite was found as a dominant mineral in some rusty precipitates from Finland. These precipitates formed in the interstices of sand grains from rapidly flowing, Fe(II)-containing water which was very quickly oxidized as it flowed through the sediment. The mineral is distinguished from other FeOOH forms and from ferrihydrite mainly by its X-ray powder diffractogram. Further characteristics are an acicular morphology (possibly thin, rolled plates), an internal magnetic field at 4°K of ~510 kOe, Fe-OH stretching bands at ~2900 cm^{-1} and Fe-OH bending bands at 1110, 920, 790, and 670 cm^{-1}, and an oxalate solubility between ferrihydrite and goethite or lepidocrocite. Feroxyhites with very similar properties were synthesized by oxidation of an Fe(II) solution with H_2O_2 at a pH between 5 and 8.

Key Words—Feroxyhite, Goethite, Infrared spectroscopy, Iron, Lepidocrocite, Mössbauer spectroscopy, Synthesis.

INTRODUCTION

In 1977 Chukhrov *et al.* described a new Fe oxyhydroxide from deep sea nodules and gley soils in the USSR which they called feroxyhite. On the basis of electron diffraction studies the structure of feroxyhite was found to be related to the ferromagnetic δ-FeOOH (Glemser and Gwinner, 1939; Bernal *et al.*, 1959; Dasgupta, 1961) but in contrast to δ-FeOOH it showed only the 4 strongest lines and was not ferromagnetic. Similar material was obtained synthetically and called δ'-FeOOH. Like ferrihydrite, the basic structure of feroxyhite is similar to hematite insofar as it consists of hexagonally close packed oxygen planes with Fe ions in the octahedral (and tetrahedral) interstices. Oxygen is partly replaced by OH and OH_2, and the degree of occupancy with Fe is less than ⅔ as it is in hematite. However, the periodicity of the octahedral sheets along the z direction varies. It is 2 for feroxyhite (c_0 = 4.60 Å) (Table 1) and 4 for ferrihydrite (c_0 = 9.4 Å) as compared to 6 for hematite (c_0 = 13.772 Å). In the case of feroxyhite the minimum a-axis can be taken as a_0, while for the better ordered δ-FeOOH, for ferrihydrite, and for hematite, an enlarged hexagonal cell with a_0 = $a(3)^{1/2}$ must be chosen (Table 1). X-ray powder diffractograms of feroxyhite and ferrihydrite are basically similar but the higher periodicity of octahedral sheets in ferrihydrite results in additional lines, of which the one at 1.97 Å is most significant and therefore diagnostic.

Feroxyhite was identified in Holocene Fe-oxides precipitated from ferriferrous groundwaters in glaciofluvial sands and gravels of Finland. It usually occurs with its two polymorphs, goethite and lepidocrocite. A number of samples from two of these localities were

chosen for more detailed characterization. In addition, Chukhrov *et al.* (1977) postulated that feroxyhite forms in nature by a rapid, abiotic oxidation of Fe at neutral to slightly acid pH. To provide more information on its genesis, a series of synhetic feroxyhites was prepared by rapid oxidation of an FeCl$_2$ solution with H_2O_2, varying pH and Fe(II) concentrations of the system similar to Misawa *et al.* (1970).

MATERIALS AND METHODS

Samples

The natural samples were collected in recently opened gravel pits where rusty Fe and black Mn oxides were precipitated from groundwater close to the present surface. The precipitates partly cement the gravel and form irregular patches with a wavy or circular internal structure, probably indicating a rapid and turbulent water flow. Locality 12 is at Parainen (60°15'N, 22°09'E) and now within a perched water table caused by underlaying bedrock. Locality 24 is at Somero (60°24'N, 23°18'E). The groundwater at Somero had an average pH of 6.9 and contained 5 mg/liter Fe. A more detailed description of this locality is given by Carlson *et al.* (1977). Samples of various colors (Table 2) were collected from the rusty precipitates.

A series of feroxyhites was synthesized by oxidizing either 0.1 M, 0.03 M, or 0.01 M FeCl$_2$ solutions with H_2O_2 (30%) at pHs between 5 and 8. In all cases a green precipitate occurred on addition of a base (NH_3 or NaOH). At pH 8 oxidation was completed within a few seconds after quickly adding an excess of H_2O_2, but the pH was not held constant. In the range of pH 7 to 5, H_2O_2 was added dropwise so that complete oxidation took about 2–3 min, and the pH could be maintained reasonably constant. The brown precipitates were filtered, washed with distilled water, and dried at room temperature.

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Table 1. Structural relationships among hematite, ferrihydrite, and feroxyhite.

		Hematite		Ferrihydrite		Feroxyhite	
Formula		α-Fe_2O_3		$Fe_2O_3 \cdot 2FeOOH \cdot 2.6H_2O$[1]		δ'-FeOOH	
Layers per unit cell $\parallel$	z	6		4		2	
Unit-cell size (Å)	a_0	5.038		5.08		2.93	
	c_0	13.772		9.40		4.60	
Characteristic XRD lines (Å)		(110)	2.519	(110)	2.54	(100)	2.54
		(113)	2.208	(112)	2.24	(101)	2.22
				(113)	1.97		
		(116)	1.6966	(114)	1.725	(102)	1.69
		(300)	1.4543	(300)	1.47	(110)	1.47

[1] After Russell (1979).

Methods

The natural samples were concentrated by isolating the fine silt and clay fractions by sedimentation in water without any pretreatment. Only the clay fraction was used because it was richer in Fe. Iron oxide minerals were identified by X-ray diffraction (XRD) using CoKα radiation and a Philips PW 1130 diffractometer equipped with a graphite diffracted beam monochromator. Samples for XRD were back-filled into aluminum sample holders and then gently pressed against filter paper to minimize orientation. Total carbon was determined with a carmograph (Wösthoff Company, Essen). In natural samples total oxidic Fe was extracted by dithionite-citrate-bicarbonate (Fe_d) (Mehra and Jackson, 1960) and in synthetic samples by concentrated HCl (Fe_t). All samples were also extracted by oxalate in the dark (Fe_o) (Schwertmann, 1964). Fe was determined by atomic absorption spectrometry using a Perkin Elmer 420 atomic absorption spectrometer. Differential thermal analysis (DTA) curves were obtained on a Linseis instrument at a heating rate of 10°C/min using hematite as an inert material. Specific surface areas were measured by the BET single point method using an Areatron automatic instrument with Ar as the adsorbing gas. Electron micrographs were obtained with a Zeiss EM 10 A/B electron microscope. Infrared spectrograms were obtained on a Beckman IR-20 A instrument using 0.3% KBr discs. Mössbauer spectra were obtained using a Co^{57}/Rh source of ~10 mCi mounted on a loudspeaker-type drive system providing a sinusoidal motion. Sample quantities of 40 mg, spread uniformly over an area of 2 cm², served as absorbers. Both source and absorber were cooled to either 124° or 4°K in a cryostat. The transmitted radiation was registered with a proportional counter and fed into a 1024 channel analyzer. Counting proceeded until a maximum of 7×10^5 to 9×10^5 counts had been accumulated per channel. The data were folded and plotted, and Lorentzian curve fits were carried out by a computer procedure.

RESULTS

Color and carbon content

The color of the natural oxides after concentration by size fractionation ranged between 7.5YR 4/8 and 7/8, becoming lighter with an increase in the proportion of goethite and lepidocrocite (Table 2). The synthetic samples were somewhat redder (5YR) and ranged in

Table 2. Properties of feroxyhite-containing natural samples.

Sample	Color	C_t	Fe_o[1]	Fe_d[1]	$Fe_{o/d}$[1]	Minerals[1]	Specific surface (m²/g)
		(%)					
12B	7.5YR 5/8	2.9	22.3	38.6	0.58	Fo > G > L	277
12C$_1$	7.5YR 4/8	2.5	16.1	36.7	0.44	Fo ≃ G > L	281
12C$_2$	7.5YR 6/8	2.5	14.4	39.6	0.36	G > Fo > L	242
12D	7.5YR 6/8	1.9	10.2	35.0	0.29	G > L > Fo	226
24A	7.5YR 5/8	0.6	22.5	40.9	0.55	G ≃ Fo	402
24B	7.5YR 6/8	1.1	15.1	42.0	0.36	G > Fo	n.d.
24C	7.5YR 7/8	0.8	8.1	36.1	0.22	G > Fo ‡ L	n.d.

[1] C_t = total carbon; Fe_o = oxalate-extractable Fe; Fe_d = DCB-extractable Fe; Fo = feroxyhite; G = goethite, L = lepidocrocite.

Table 3. Properties of synthetic feroxyhites.

| Sample | Conditions of preparation | | | Properties[1] | | | | X-ray powder diffraction data | | | | | | | |
| | pH | Fe(II) (Molarity) | Color | Fe_o (%) | Fe_t (%) | $Fe_{o/t}$ | Spec. surf. m^2/g | (100) | | (101) | | (102) | | (110) | |
								d (Å)	WHH[2] (°2θ)	d (Å)	WHH (°2θ)	d (Å)	WHH (°2θ)	d (Å)	WHH (°2θ)
PC 4	8	0.10	5YR 5/8	22.6	54.0	0.42	143	2.563	0.60	2.231	0.95	1.70	1.48	1.477	1.10
PC 5	8	0.03	5YR 5/8	30.3	55.4	0.55	187	2.560	0.80	2.239	1.25	1.70	2.00	1.478	1.10
PC 6	8	0.01	5YR 4/9	31.3	53.5	0.58	198	2.557	0.82	2.234	1.70	1.70	3.80	1.476	1.15
PC10	6	0.10	5YR 4/9	33.7	52.4	0.64	265	2.557	0.75	2.239	2.25	1.70	3.90	1.474	1.25
PC 9	6	0.03	5YR 4/9	42.6	52.3	0.81	305	2.543	0.95	2.234	1.90	1.70	4.80	1.472	1.40
PC16	5	0.03	5YR 4/8	45.8	51.1	0.90	298	2.545	1.90	2.239	1.70	1.70	n.m.[3]	1.473	2.10
PC19	5	0.01	5YR 4/8	50.4	52.3	0.96	240	2.539	2.30	2.248	2.70	1.70	n.m.	1.472	2.50

[1] Fe_o = oxalate-extractable Fe; Fe_t = total Fe.
[2] Width at half height (uncorrected).
[3] Not measurable.

value between 4 and 5 and in chroma between 8 and 9 (Table 3). In series 12 the total carbon content decreases with increasing proportion of goethite and lepidocrocite (Table 2). This supports the idea that organic compounds prevented or retarded the formation of better crystalline Fe-oxides (Schwertmann *et al.*, 1968). In series 24, however, this correlation does not exist.

X-ray powder diffraction

As seen from XRD traces (Figure 1), sample 12B contains the highest proportion of feroxyhite. It can be identified by four strong lines at 2.53, 2.23, 1.71, and 1.46 Å, which are also visible on selected area electron diffractograms (not shown). The four feroxyhite lines show a marked line broadening following the order (100) ~ (110) < (101) < (102). This is in agreement with the synthetic samples and is discussed below. Small amounts of goethite (4.17 Å) and lepidocrocite (6.27, 1.94 Å) as well as quartz and feldspars are also present. More goethite and lepidocrocite are present in the other three samples of series 12 ($12C_1$, C_2, D in Figure 1). The diffractograms of the samples of locality 24 (not shown) show the same type of mineral association but with less feroxyhite.

The main feroxyhite peak at 2.53 Å exhibits a strong asymmetry towards lower angles. This could be due to a very broad asymmetric peak at ~2.5 Å, which together with a less intensive peak at ~1.5 Å is characteristic of very poorly ordered Fe-oxides, similar to the 4-Fe(O,OH) octahedra units of Feitknecht *et al.* (1973). This type of material is common in connection with ferrihydrite and can be considered a very poorly ordered form of ferrihydrite (Chukhrov *et al.*, 1973; Carlson and Schwertmann, 1980) but it can equally well be considered as a poorly ordered form of feroxyhite. The four characteristic lines of feroxyhite show up in the XRD patterns of all synthetic samples (Figure 2). Because the structure of feroxyhite is related to ferrihydrite (see Introduction), the d-values of these four lines are similar

to those of ferrihydrite, but the absence of the 1.97-Å line characteristic of ferrihydrite distinguishes the two compounds (Chukhrov *et al.*, 1977). The best crystallized samples (e.g., PC 4) have an additional, very broad reflection at about 3.1 Å also observed by Chukhrov *et al.* (1977) which can not yet be accounted for. The same asymmetry of the 2.54-Å peak towards lower angles as observed in the natural sample occurs in most of the synthetic samples as well (Figure 2). The proportion of very poorly ordered material indicated by this asymmetry increases with decreasing crystallinity (see also $Fe_{o/t}$). A small peak at 1.94 Å is due to a trace of poorly crystalline lepidocrocite which usually does not show the strongest peak at 6.27 Å (Schwertmann and Taylor, 1979).

As revealed by line broadening (Table 3), the synthetic feroxyhites become less crystalline as the Fe(II) concentration and the pH drop. With decreasing crystallinity the (100) line shifts from 2.563 to 2.539 Å and the (110) line from 1.477 to 1.472 Å (Table 3). No explanation for this can be given yet. Chukhrov *et al.* (1977) observed a sensitivity of the d values to degree of ordering. Pronounced differential line broadening indicates anisotropic crystal growth. Line width generally follows the order (100) ~ (110) < (101) < (102), this order being more expressed the lower the crystallinity. In fact, in the most poorly crystalline sample the (102) line is virtually absent. This is in accordance with the observations of Chukhrov *et al.* (1977) and indicates an extreme thinness of the platy crystals. An analogous situation has been observed with poorly crystalline hematites (Schwertmann *et al.*, 1979).

Oxalate solubility

Many experiments have shown that the proportion of Fe extracted by a 2-hr treatment with 0.2 N NH_4 oxalate at pH 3.0 in the dark and with a ratio of <2 mg Fe/ml oxalate varies strongly among the various Fe oxide minerals in soils. Goethite and hematite are virtually
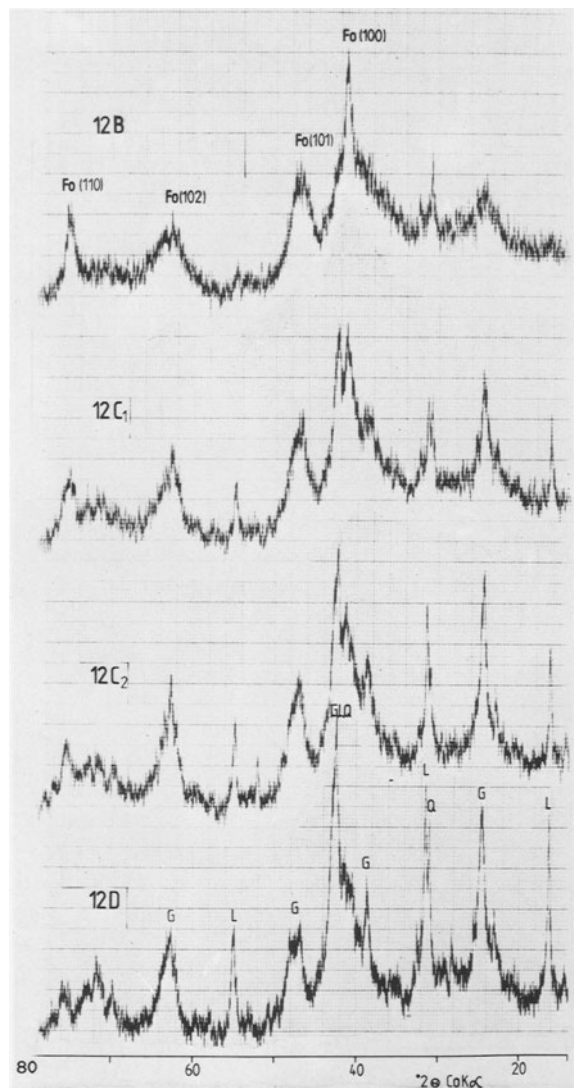
Figure 1.   X-ray powder diffractograms of natural feroxyhite containing samples (Fo = feroxyhite, G = goethite, L = lepidocrocite, Q = quartz).

Figure 2.   X-ray powder diffractograms of synthetic feroxyhites.

insoluble; lepidocrocite is very slightly soluble; whereas ferrihydrite is almost completely soluble. Nothing is known so far about feroxyhite. Sample 12B with the highest proportion of feroxyhite shows an $Fe_{o/d}$ of 0.58 (Table 2). This value is probably high because of the presence of some very poorly ordered, oxalate soluble Fe oxides. To test the oxalate solubility of a natural feroxyhite, sample 12B was extracted three times for 2 hr each with oxalate and X-rayed after each treatment. From the changes of the height of the XRD peaks of feroxyhite at 1.46 Å, goethite at 1.72 Å, and lepidocrocite at 6.27 Å measured relative to the quartz peak at 3.34 Å, the proportion dissolved was calculated. In the first extraction about 30% of the feroxyhite, about 15%
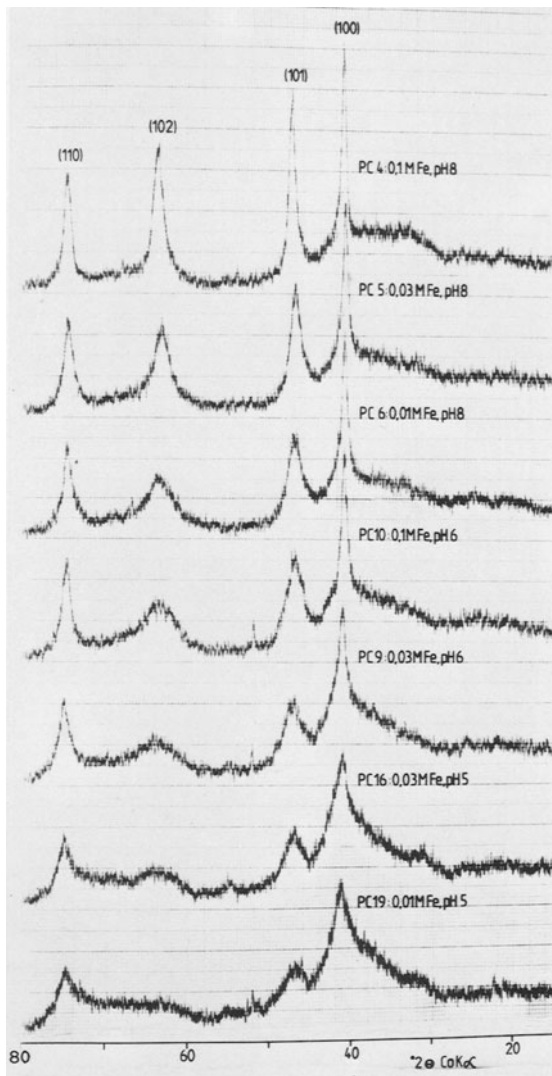
of the lepidocrocite, and no goethite were dissolved. After 3 extractions about 85% of the feroxyhite, 50% of the lepidocrocite, and 10% of the goethite were dissolved. Feroxyhite is thus more soluble than goethite and lepidocrocite but less soluble than ferrihydrite which has an $Fe_{o/t}$ of ~1 (Schwertmann and Fischer, 1973).

The synthetic samples show a range of solubilities in oxalate (Table 3). The best crystallized one has an $Fe_{o/t}$ of 0.42. With decreasing crystallinity, the $Fe_{o/t}$ rises to 0.96. There is a significant correlation between line width and $Fe_{o/t}$ (e.g., for the (100) line: r = 0.88, n = 12). Although this relation underlines how crystallinity may influence the solubility, the greater part of this in-

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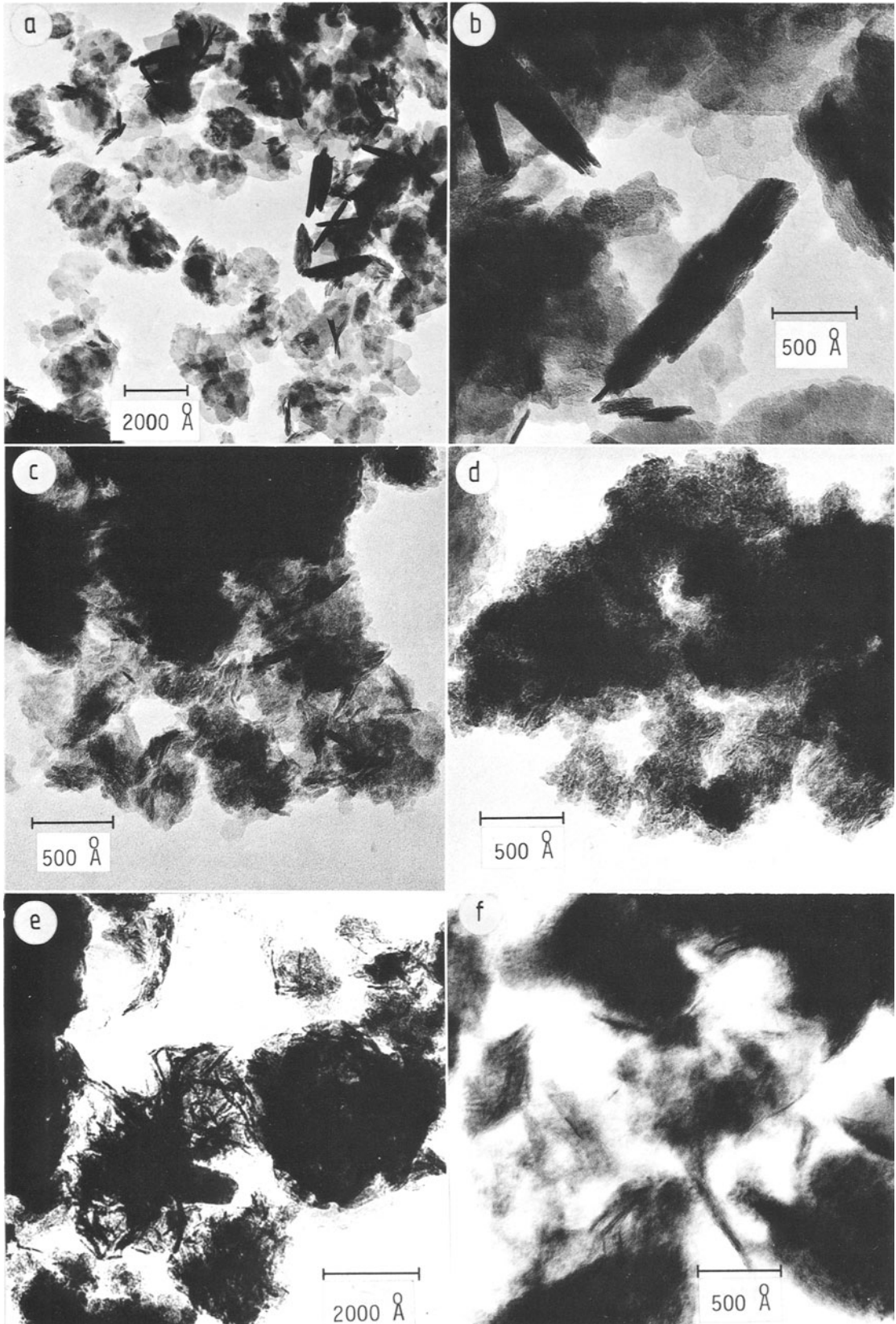
crease is believed to be due to increasing proportions of very poorly ordered material as discussed earlier.

Particle size and morphology

Specific surface areas between 226 and 277 m²/g (Table 2) indicate the small particle size of the natural Fe-oxides. Goethite and lepidocrocite in these samples appear to have slightly larger particles because the specific surface decreases when their proportion increases (from sample 12B to sample 12D). The surface area of synthetic feroxyhites increased from 143 to 305 m²/g as crystallinity decreased (Table 3). A decrease in the two last members, although crystallinity further decreased, is most probably due to strong aggregation of the very fine particles, making part of the surface inaccessible to the adsorption gas. The same was observed with natural and synthetic ferrihydrites (Schwertmann and Fischer, 1973; Carlson and Schwertmann, 1980).

The needle-like appearance of the natural feroxyhite particles (Figures 3e, 3f) is in accordance with Chukhrov et al. (1977) who considered them as thin, rolled plates. In addition, higher proportions of very small, aggregated spherical particles are common; these may be considered as poorly crystallized ferrihydrite, in agreement with XRD data. As expected from XRD, the electron micrographs of the synthetic feroxyhites show a range of crystallinities. The best crystallized sample (PC 4, Figures 3a, 3b) shows very thin, partly hexagonal flakes (Feitknecht et al., 1969) but also needle-like particles which also may be rolled plates. The extreme thinness of these flakes is reflected in the differential line broadening of the XRD peaks which indicate that the flakes lie on the (001) plane. The sample with medium crystallinity (PC 9, Figure 3c) is slightly less crystalline than the natural sample and has a somewhat similar morphology consisting of needle-like crystals. In the most poorly crystallized sample (PC 19, Figure 3d), the acicular nature of the crystals is barely visible, and spherical particles are common, in agreement with the higher proportion of very poorly ordered Fe-oxide (see XRD, Figure 2).

Infrared absorption (IR)

Due to low crystallinity, IR spectra are not very well developed. The best crystallized synthetic sample (PC 4) shows, besides the features for molecular water, a shoulder at 2900 cm⁻¹ (OH stretching) and weak broad bands at 1115, 910, 790, and 670 cm⁻¹ due to Fe-OH-bending (Figure 4). Features at 430 and 300 cm⁻¹ may be assigned to Fe-O-bonds. This spectrogram is in general agreement with those of Feitknecht et al. (1969),
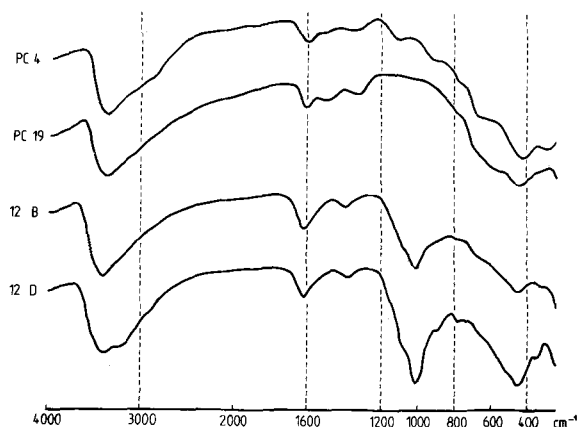

Figure 4.   IR spectrograms of two synthetic feroxyhites (PC 4, PC 19) and two natural feroxyhite-containing samples (12B, 12D).

Misawa et al. (1970) and Chukhrov et al. (1977). After oxalate treatments the bands are somewhat better expressed. Heating to 80°C for 1 hr does not improve the spectrum of sample PC 4, and heating to higher temperatures is not feasible because of phase transformations (Povitskii et al., 1976). All bands become weaker as crystallinity decreases and finally almost disappear (see sample PC 19) (Figure 4).

The features in the natural sample (12B) are similar but less pronounced than in sample PC 4 because of lower crystallinity and purity (Figure 4). A band at 1400 cm⁻¹ may be due to COO-groups, and bands in the 1200–900 cm⁻¹ range, partly masked by a strong broad band at 1015 cm⁻¹, are probably due to clay silicates and some Si-O-Fe bonds as discussed elsewhere (Schwertmann and Thalmann, 1976; Carlson and Schwertmann, 1980). Further interference (790 and 900 cm⁻¹) comes from traces of goethite and lepidocrocite as indicated by the spectrograms of those samples of series 12 which contain substantial amounts of these two materials (e.g., sample 12D).

Thermal behavior

Differential thermograms of sample 12B under an N₂ atmosphere show a strong, double endothermic peak at 150° and 200°C and a weak endothermic peak at about 400°C. A very broad and weak exotherm between 500° and 900°C appears to be connected with the slow decomposition of organic matter due to small amounts of O₂ in the N₂ used. Increasing amounts of goethite and lepidocrocite (samples 12C, 12D) are reflected in two endothermic peaks at 255–263° and 280–288°C.

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Figure 3.   Electronmicrographs of synthetic feroxyhites of good (3a, b: sample PC 4), medium (3c: sample PC 9) and low (3d: sample PC 19) crystallinity and of natural feroxyhite (3e, f: sample 12B).
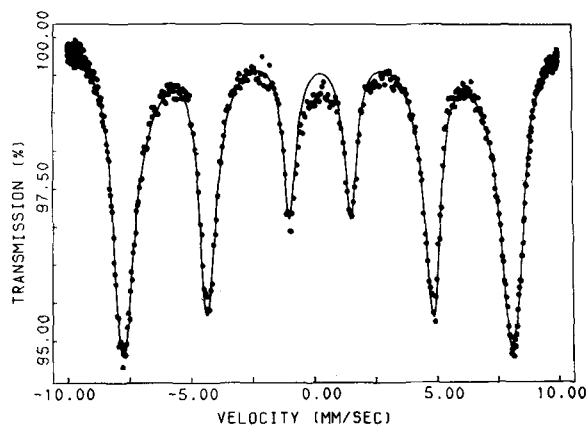
Figure 5. Mössbauer spectrum of an impure natural feroxyhite (sample 12B).

Table 4. Ratio of half-height width of (104) to (110) at various temperatures.

	240°C	290°C	410°C
Sample PC 4	5.6	4.2	3.0
	250°C	270°C	350°C
Sample PC 9	3.4	2.8	1.5

DTA runs were interrupted to obtain further information on phase transformations by XRD. If interrupted at 190°C and 260°C, the feroxyhite is unchanged, except that at 260°C the XRD peaks are somewhat stronger and sharper and have significantly shifted to lower d values. Using the (110) and (300) line of feroxyhite and the quartz line at 3.34 Å in the sample as an internal standard, a shift of a_0 of the hexagonal unit cell from 5.062 Å to 5.027 Å was found, indicating a slight shrinkage of the unit cell by heating. Interrupted at 460°C, feroxyhite is still dominant (with a_0 the same as at 260°C), but a small amount of hematite and maghemite has also formed. Maghemite is the sole phase if the sample is heated to ~800°C under limited air supply. As described earlier (Schwertmann and Heinemann, 1959) Fe-oxides containing organic matter convert to maghemite in an N_2 atmosphere.

If, however, sufficient air is supplied, the organic matter (2.9% C_t) is oxidized as indicated by a strong exothermic peak between 300° and 500°C. At 550°C, i.e., shortly above the exothermic peak, the sample consists predominately of strongly disordered hematite (with possibly some feroxyhite), but after heating to 900°C, well-ordered hematite is obtained. This indicates that if the organic matter is oxidized, no maghemite forms, but the formation of well-ordered hematite is still hindered. A similar phenomenon was observed with natural ferrihydrites and it was shown that this hindrance was due to adsorbed silicate in the sample (Carlson and Schwertmann, 1980). Among the synthetic feroxyhites only the best crystallized one, sample PC 4, showed a clear endothermic peak at 260°C (besides the dehydration peak). With decreasing crystallinity this peak appears to be overcompensated by one or two exothermic peaks.

XRD traces were run on samples PC 4 and PC 9 at various temperatures of interruption. Even at the lowest temperature, 240–250°C, both samples were already converted to hematite, in contrast to the natural feroxyhite. This hematite however, showed strong differential line broadening, with (110), (113), (116), and (300) being much sharper than (012), (104), (024), and (214). This phenomenon was also observed by Francombe and Rooksby (1959) during the transformation of goethite to hematite by heating. They explained this as a take-over of a structural subunit from goethite by hematite, with those planes that are common to both phases yielding sharp lines. The broader lines correspond to a disordered superstructure of those units, i.e., to planes newly formed in the hematite structure. Further heating produces a fully ordered structure and equally sharp XRD lines. The disorder at low temperatures can be simply characterized by the ratio of the width at half height (WHH) of the (104) to that of the (110) line. This ratio decreases for the two samples with temperature of interruption, asymptotically approaching unity (see Table 4). Obviously, the less well-crystallized sample, PC 9, attains a certain degree of ordering at a temperature lower than the better crystallized sample PC 4. Generally, the exothermic peak seems to be due to an increase in crystallinity of hematite.

Mössbauer data[2]

At 124°K the Mössbauer spectrum of sample 12B consists of a broad Fe^{3+} doublet, a subordinate Fe^{2+} doublet, and a weak, magnetically split sextet. At 4°K (Figure 5) the paramagnetic components have practically disappeared, and the spectrum consists of very broad, magnetically split lines. A three-sextet model gave hyperfine fields of 510, 488, and 447 kOe. The 510-kOe field is similar to the field for the synthetic feroxyhite, sample PC 4, which amounts to 513 kOe. In agreement with XRD, the field of 447 kOe could be due to a small amount of lepidocrocite, whereas the field of 488 kOe might be attributed to poorly ordered goethite and/or ferrihydrite.

Genesis

The presence of Fe(II) compounds in the Fe-bearing waters from which feroxyhite was formed, and the

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presence of lepidocrocite in most samples indicate that the feroxyhite was formed from the oxidation of Fe(II) compounds. The rate of oxidation must have been very high and can be simulated by strong oxidants such as H_2O_2. At lower oxidation rates lepidocrocite and/or goethite will be the primary products.

Synthetic δ-FeOOH has usually been prepared by the oxidation of Fe(OH)$_2$ (Glemser and Gwinner, 1939; Feitknecht et al., 1969; Povitskii et al., 1976) or from soluble Fe(II) hydroxy complexes (Misawa et al., 1970). This involves a rather high pH rarely occurring in nature. However, Chukhrov et al. (1977) pointed out that feroxyhite can be obtained by H_2O_2 oxidation of a Fe(II) solution even at pH 6–6.5 if silica is present. The present experiments show that even in pure systems feroxyhite forms at pH values as low as 5. It is therefore entirely possible that feroxyhite is formed in nature where the oxidation of Fe(II) is rapid. This requires that the Fe(II) be in an easily oxidizable form and that the rate of air supply be high. This appears to be the case where ferriferous waters run through highly porous, sandy sediments close to the surface, and it is here where feroxyhite has been found in Finland. In contrast, ferrihydrite is commonly formed where groundwater discharges onto the surface (Carlson and Schwertmann, 1980). It seems likely that lepidocrocite and goethite in these samples were not formed through a transformation of feroxyhite but also directly from solution by slower oxidation of Fe as suggested from synthesis experiments (Schwertmann and Thalmann, 1976).

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Резюме—Фероксигит (δ'-FeOOH) в ассоциации с гетитом и лепидокроцитом оказался преобладающим минералом в ожелезненных осадках из Финляндии. Эти осадки отложились между зернами песка из быстротекущей воды, содержащей Fe(II), которая очень быстро окислялась при прохождении через эти отложения. Этот минерал отличается от других форм FeOOH и от ферригидрита в основном своей рентгеновской порошковой дифрактограммой. Добавочными характеристиками являются игольчатая морфология (возможно тонкие свернутые пластинки), внутреннее магнитное поле, которое при 4°К составляет 510 кОе, растянутые полосы Fe-OH при ~2900 см$^{-1}$ и сгибающиеся полосы Fe-OH при 1110, 920, 790, и 670 см$^{-1}$, и оксалатная растворимость между ферригидритом и гетитом или лепидокроцитом. Фероксигит с очень похожими свойствами был синтезирован окислением раствора Fe(II) с помощью H$_2$O$_2$ при pH между 5 и 8. [N.R.]

Resümee—Feroxyhit (δ'-FeOOH) wurde, vergesellschaftet mit Goethit und Lepidokrokit, als dominierender Bestandteil ockerfarbener Ausfällungen in Finnland gefunden. Er hat sich durch schnelle Oxidation Fe-haltiger Wässer in porösen sandigen Sedimenten gebildet. Das Mineral unterscheidet sich von den anderen FeOOH-Formen und vom Ferrihydrit hauptsächlich durch sein Röntgendiagramm. Weitere Kennzeichen sind eine nadelige Kristallform (vermutlich aufgerollte dünne Blättchen), ein inneres Magnetfeld bei 4°K von 510 kOe, Fe-OH-Valenzschwingungen bei 2900 cm^{-1} und Fe-OH-Knickschwingungen bei 1100, 920, 790, und 670 cm^{-1} und eine Oxalatlöslichkeit zwischen Ferrihydrit und Lepidokrokit und Goethit. Feroxyhite mit sehr ähnlichen Eigenschaften wurden durch Oxidation von Fe(II)-Lösungen mit H$_2$O$_2$ bei pH 5–8 synthetisiert.

Résumé—On a trouvé que la feroxyhite (δ'-FeOOH) associé à la goethite et la lepidocrocite était un minéral dominant dans quelques precipitées rouillés de Finlande. Ces précipités s'étaient formés dans les interstices de grains de sable, à partir d'eau contenant du Fe(II) s'écoulant rapidement, et qui etait très vite oxidée tandis qu'elle coulait à travers le sédiment. Ce minéral peut principalement être distingué d'autres formes de FeOOH et de la ferrihydrite par son diffractogramme aux rayons-X. D'autres caractéristiques sont une morphologie aciculaire (possiblement de fines plaques enroulées), un champ magnétique interne à 4°K d' ~510 kOe, des bandes d'étirement Fe–OH à ~2900 cm^{-1} et des bandes de courbure à 1110, 920, 790, et 670 cm^{-1}, et une solubilité oxalate entre la ferrihydrite et la goethite ou la lepidocrocite. Des feroxyhites ayant des propriétés très semblables ont été synthetisées par oxidation d'une solution Fe(II) avec du H$_2$O$_2$ à un pH entre 5 et 8. [D.J.]