Clays and Clay Minerals, Vol. 52, No. 2, 221–226, 2004.

FORMATION AND PROPERTIES OF A CONTINUOUS CRYSTALLINITY SERIES OF SYNTHETIC FERRIHYDRITES (2- TO 6-LINE) AND THEIR RELATION TO FeOOH FORMS

Udo Schwertmann*, Josef Friedl and Andreas Kyek
Institut für Bodenkunde, Technische Universität München, D-85350 Freising-Weihenstephan, Germany

Abstract—Ferrihydrite is a poorly crystalline Fe oxide of which 2-(XRD)line and 6-line varieties are commonly used in experiments, although species with intermediate numbers of peaks have been found in nature. To simulate nature, we synthesized two continuous series of ferrihydrites with between 2 and 6–7 peaks at room temperature in two different ways: (1) by varying the rate of hydrolysis of an $Fe(NO_3)_3$ solution (HR series); and (2) by oxidizing an $FeCl_2$ solution containing up to 73 mmol Si/L (Si series), both at pH 7. Mössbauer spectra at 4.2 K showed that the ferrihydrites of the HR series had a constant magnetic hyperfine field (B_{hf}) at 4.2 K of 48.8 T whereas B_{hf} in the Si series dropped from 49.4 to 46.7 T as the Si content of the ferrihydrites increased from 0 to 74.7 g/kg of Si. Temperature scans between 4 and 170 K illustrate that the magnetic order breaks down at a temperature which is lower the higher the hydrolysis rate and the Si concentration in the ferrihydrite.

Key Words—2-6 line Ferrihydrite, Mössbauer, Si, Synthesis, XRD.

INTRODUCTION

Ferrihydrites are a group of poorly crystalline, high-surface area Fe oxide minerals with somewhat variable composition with respect to the H_2O-OH/Fe ratio. Two varieties are usually synthesized. They are called 2- and 6-line ferrihydrite (2L-Fh; 6L-Fh) on the basis of their two or six broad X-ray diffraction (XRD) peaks. The 2-line variety (often called 'hydrous ferric oxide', HFO, (Dzombak and Morel, 1990; Janney *et al.*, 2000a, 2000b)) is synthesized by rapid hydrolysis of an Fe^{III} salt solution at circumneutral pH, whereas the 6-line variety forms when an $Fe(NO_3)_3$ or $Fe(ClO_4)_3$ solution is heated for 12 min at 75–85°C and then dialyzed against distilled water. In contrast, in natural surface environments, intermediate forms with between two and six XRD peaks have been reported from various soils (gleys, podsols, andosols), hot and cold springs, lakes, creeks and acid mine waters (for a review see Carlson and Schwertmann, 1981; Cornell and Schwertmann, 2003).

Mössbauer spectroscopy has been used successfully to characterize ferrihydrites. At room temperature (RT) natural and synthetic samples are superparamagnetic and their spectra show asymmetrically broadened quadrupole splittings of maximum probability which correspond to the average Fe^{3+} site distortion (Murad, 1996). These ranged 0.75–0.86 mm/s for 2L- and 0.62–0.71 mm/s for 6L-ferrihydrites (Murad and Schwertmann, 1980; Murad *et al.*, 1988). Temperature scans reveal magnetic blocking temperatures, T_B, of 28 K for a 2L and 45 and 115 K for two different 6L samples (Murad *et al.*, 1988). These data demonstrate the particular strong superparamagnetic relaxation of ferrihydrites due, for pure samples, to their low crystallinity. In addition, natural ferrihydrites often contain substantial amounts of coprecipitated C (humics) and Si, and such diamagnetic impurities may further interfere with the spin orientation of the Fe atom. In conclusion, in addition to XRD, Mössbauer spectroscopy is well suited to further characterize ferrihydrites.

A systematic study of hyperfine magnetic properties of synthetic ferrihydrites within the full range of crystallinity between 2 and 6 XRD peaks has not yet been done. Such a continuum in crystallinity suggests a genetic relationship of some kind between the different varieties. The nature of this relationship is not clear. It may be that better crystalline forms develop from less crystalline precursors by 'ageing', or, alternatively, each variety reflects a slightly different means and/or environment of formation. The latter was demonstrated by Lewis and Cardile (1989). They kept 10^{-4}–10^{-2} M $Fe(NO_3)_3$ solutions for between 30 s and 17 h at RT and pH of 2.2–3.2 before completing the hydrolysis and coagulating the product by quickly raising the pH to 7 with NaOH. In this way, they obtained 2L-Fh after quick hydrolysis and 6L-Fh together with some FeOOH (lepidocrocite, goethite) at slow hydrolysis. This suggests a separate formation of the different forms due to a kinetic factor. It is clear, however, that in nature the better crystalline ferrihydrite does not form at very low pH. Another factor which is more likely to cause the range in crystallinity is the presence of dissolved compounds which affect crystallization.. Because Si usually occurs in aqueous natural systems and because natural ferrihydrites usually contain Si (Carlson and Schwertmann, 1990), we speculate that dissolved Si may also affect the different forms.

---

* E-mail address of corresponding author:
uschwert@wzw.tum.de

DOI: 10.1346/CCMN.2004.0520208

With these facts in mind, a more systematic study was conducted, in which natural conditions were further approached by: (1) avoiding strongly acid conditions and elevated temperatures in an Fe^{III}-system; (2) using, besides Fe^{III}, also Fe^{2+} as the Fe form from which ferrihydrite forms in surface environments; and (3) including the effect of soluble Si as a potentially interfering compound.

MATERIALS AND METHODS

Synthesis of the samples

Hydrolysis (Fe^{III}) series (ser. 74). 50 mL of a 0.1 M $Fe(NO)_3$ solution (5 mmol Fe) were automatically titrated with 15 mmol NaOH to pH 7 at RT under vigorous stirring. To vary the rate of hydrolysis, the NaOH concentration was varied between 7.7×10^{-4} and 1 M in eight steps and a constant rate of NaOH addition of 1 mL/min (dropwise) yielding a time range for total neutralization of between 0.25 and 130 h and a corresponding rate of OH addition (hydrolysis rate HR) of between 0.38 and 200 μmol OH $mmol^{-1}$ Fe min^{-1}. After complete hydrolysis (OH/Fe = 3), the solids were separated by centrifugation, washed with 70 mL of distilled water, dried at 40°C and ground gently.

Silicate (Fe^{II}) series (ser. 75). 50 or 100 mL of a filtered 0.1 M $FeCl_2$ solution were oxidized at RT and pH 6.5 in an open vessel under vigorous stirring (Schwertmann and Cornell, 2000, p. 78) in the presence of dissolved silicate. The pH was kept constant with the help of an automatic titrator by the addition of 0.3 M NaOH being 0 to 73 mmolar in dissolved Si (from Na silicate) in nine steps. The NaOH was kept CO_2-free with a trap. Complete oxidation took ~2–7 h and tended to take longer as the Si concentration increased. The idea to combine the silicate with the addition of a base to neutralize the protons during oxidation was to guarantee a continuous flow of Si while the ferrihydrite is formed as expected in a natural environment. A separate experiment had shown that if Si was added at the beginning of the oxidation, crystalline lepidocrocite was predominantly formed indicating that Si had no inhibiting effect on the product, probably because the first ferrihydrite formed retained the silicate and, thereby, purified the solution. After complete oxidation (duration of 2–4 h) the solids were treated as above.

Sample characterization

The samples were analyzed for total Fe and Si by atomic absorption spectroscopy after complete dissolution in 3 M HCl. The surface area was determined from 7 or 11 adsorption points in the p/p_0 range between 0.05 and 0.3 using an AUTOSORB-1 instrument (Quantachrome) with N_2 as the adsorbate. The multipoint BET of the Quantachrome software was applied. Samples were outgassed at 70°C and ~40 mbar for at least 2 h. X-ray diffraction patterns were recorded from backfill powder mounts using CoKα radiation and a Philips PW 1070/1820 goniometer equipped with a diffracted-beam monochromator and a 1° divergence slit. Specimens were step scanned from 10 to 80°2θ in increments of 0.05°2θ and with 20 s counting time. The broad peaks were fitted with an experimental fit procedure as described elsewhere (Stanjek and Schwertmann, 1992) to obtain line position and width. Due to the low crystallinity of the product, the background is high (see the vertical bars in Figure 1). The experimental fit procedure does not take into account the background but fits a somewhat artificial base line to the traces. This has no effect on the fitted line positions but underestimates the line width.

Mössbauer spectra were recorded at RT and 4.2 K using a sinusoidal acceleration spectrometer, with sources of ^{57}Co in Rh and an α-Fe foil for calibration. The spectra were fitted with sets of split Gaussian distributions of Lorentzian-shaped lines for the magnetic sextets and quadrupole doublets as described by Friedl and Schwertmann (1996). Based on their phase-specific magnetic hyperfine fields, the different Fe oxides were quantified according to their area proportion of the sextet. For further characterization, their magnetic behavior spectra were also recorded at temperatures between 4.2 and 170 K (temperature scan). Bath or gas-flow cryostats were used for temperature adjustment.

RESULTS AND DISCUSSION

Hydrolysis rate series

The total Fe content (Table 1) of the ferrihydrites in an air-dried state is uniform around 580 g/kg and decreased somewhat as the hydrolysis rate increased. The surface area (SA) reflects the mineralogy but also the physical state of the samples. A maximum of 276 m^2/g occurred where the ferrihydrite showed a full 6-line pattern and no FeOOH had formed and the two lowest SA values occurred at the two highest HRs, *i.e.* where the crystallinity/particle size of the ferrihydrite were lowest. This is probably due to an increasingly stronger aggregation, or, alternatively, to strongly adsorbed water, both of which make the particle surface less accessible to N_2 adsorption. Underestimation of SAs seems a common phenomenon in ferrihydrites (Jambor and Dutrizac, 1998).

The XRD traces (Figure 1, left) show that between a HR of 333 and 16.7 μmol OH/min, ferrihydrites were the sole phases formed. As the HR decreased within this range, the complete series from a 2-line form with incipient indication of more peaks to a 6-line form as first shown by Towe and Bradley (1967) and later by others (Chukhrov *et al.*, 1973; Eggleton and Fitzpatrick, 1988; Drits *et al.* 1993) for 6-L ferrihydrite occurred. As their number grew, the peaks also became sharper. Using the width of the 110 peak and the Scherrer formula, the

Table 1. Properties of Fe oxides formed by hydrolyzing 0.1 M $Fe(NO_3)_3$ solutions at different rates.

Rate of hydrolysis	Surface area	Total Fe	Minerals[1]			FWHH[2] of $Fh_{(110)}$		Hyperfine properties at 4.2 K			
								Ferrihydrite		Lepidocrocite	
			Fh	Lp	Gt		$B_{hf}(av)$	$B_{hf(prob)}$	ΔE_Q	B_{hf}	ΔE_Q
μmol OH/min	m^2/g	g/kg	%			°2θ		T	mm/s	T	mm/s
0.65	229	589	46	41	13	n.m.[3]	48.73	51.4	−0.028	44.31	0.045
1.7	n.d.	586	63	28	9	3.56	48.88	51.0	−0.022	44.51	0.066
2.8	244	575	80	20	0	4.11	48.66	50.7	−0.066	–	–
5.5	256	584	83	17	0	4.32	48.92	50.5	−0.058	–	–
16.7	239	579	100	0	0	4.45	48.88	50.5	−0.042	–	–
33.3	276	557	100	0	0	4.99	48.81	50.4	−0.037	–	–
66.7	227	555	100	0	0	5.27	48.86	50.4	−0.024	–	–
333	214	535	100	0	0	7.01	48.87	50.6	−0.011	–	–

[1] based on Mösbauer spectroscopy; Fh – ferrihydrite; Lp – lepidocrocite; Gt – goethite
[2] full width at half height
[3] not measurable

crystal size increased from 1–2 nm to ~4 nm. Although in the range given for ferrihydrites (*e.g.* Murphy *et al.*, 1976; Janney *et al.*, 2000a) this is probably an underestimation because it ignores the influence of crystal disorder on peak broadening. No change in peak position could be ascertained.The weak peaks at >0.3 nm appearing at a HR of 5.5 μmol OH/min are not due to ferrihydrite but to small amounts of rather poorly crystalline lepidocrocite and goethite of which lepidocrocite finally dominates as the HR drops further. As seen from its pronounced anisotropic line broadening (peak width of 020 >> 002), the lepidocrocite consists of very thin laths, typical for its low crystallinity (Schwertmann and Taylor, 1979; Kämpf and Schwertmann, 1983).

All Mössbauer spectra taken at 4.2 K show a sextet indicating that at this temperature the Fe^{III} spins in even the most disordered oxide (2L-Fh) are completely frozen (Figure 2). The dips of the sextets are asymmetric towards lower velocities showing a range of hyperfine fields. To characterize this, two hyperfine fields (B_{hf}) are given in Table 1, viz. the average field, $B_{hf}(av)$, and the field of maximum probability, $B_{hf}(prob)$. Whereas the $B_{hf}(av)$ of ferrihydrite is uniformly at 48.8 T, the $B_{hf}(prob)$ at ~50–51 T shows a weak increase with increasing crystal order. In other words, as more FeOOH is formed, the crystallinity of the ferrihydrites also increased, thereby reflecting the improved conditions for crystallization. More pronounced is the trend of the quadrupole split, ΔQ, which drops from −0.011 to

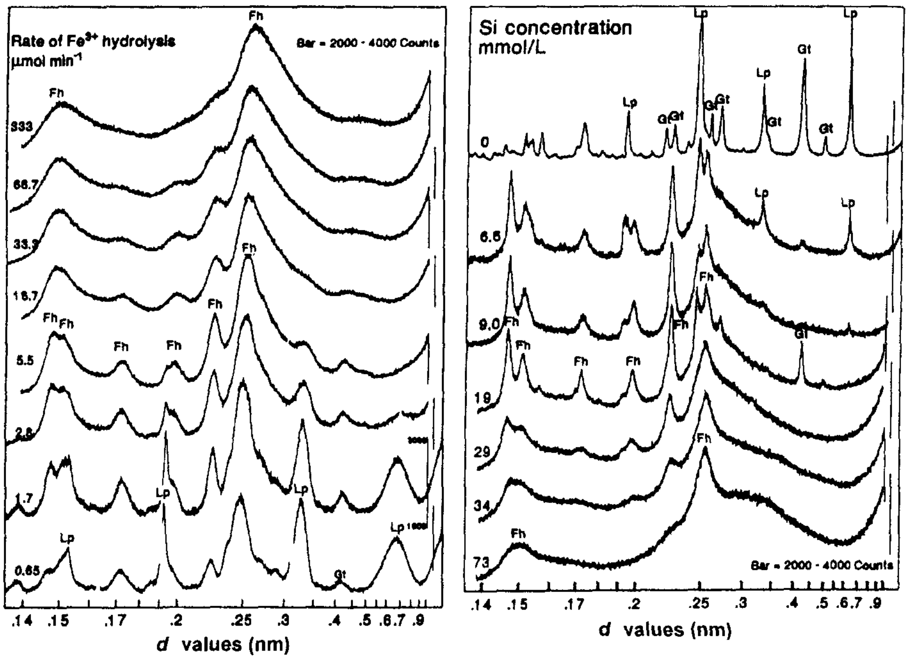

Figure 1. XRD patterns of the Fe oxides formed at RT and at pH 7 by hydrolyzing a 0.1 M $Fe(NO_3)_3$ solution at various rates (left) and by oxidizing with air a 0.1 M $FeCl_2$ solution containing various Si concentrations (right).

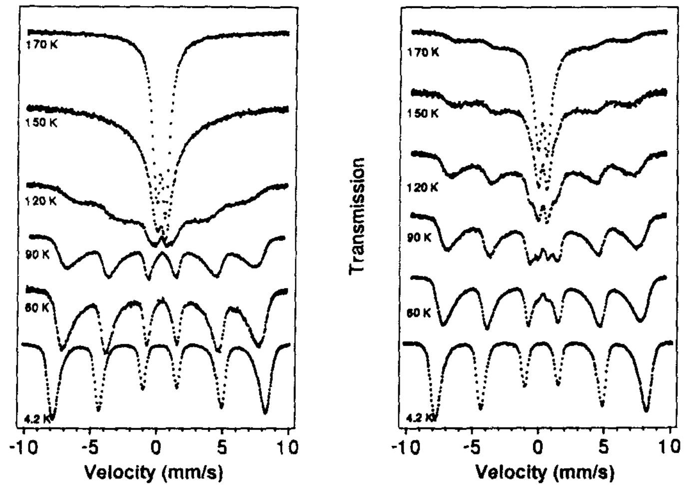

Figure 2. Mössbauer spectra of two 6-line ferrihydrites produced by oxidizing a 0.1 M $FeCl_2$ solution containing 9.0 mmol L^{-1} Si (left) compared with the standard 6-line ferrihydrite (6-LFh) produced after Towe and Bradley (1967) by hydrolyzing an acid $Fe(NO_3)_3$ solution at 85°C (right).

0.066 mm/s as the structural order increases. The crystal order of the ferrihydrites is also reflected in the dependency of the B_{hf}(av) on the temperature at which the samples are recorded (temperature scan). Figure 3 shows that the decrease of B_{hf}(av) is stronger with lower crystal order. Compared with standard 2L- and 6L-Fh, which are also shown, our samples show a slightly more rapid decay of their magnetic order. Note that the 6L-Fh of the silicate series (see next section), also shown in Figure 3, shows the weakest decay of magnetic ordering suggesting an even better order than the standard 6L-Fh.

Fe^{II}-silicate series

Parallel to the Si concentration in solution, the Si content of the air-dried precipitates increased from 0 to 74.7 g/kg corresponding to an Si/(Si+Fe) mole ratio of 0.257. The linear correlation between the Si concentration in solution and the Si/(Si+Fe) mole ratio in the product is highly significant ($r = 0.950$) if the highest Si concentration is omitted. For the latter, the Si/(Si+Fe) mole ratio ranged significantly below the regression line which indicates that the capacity of the Fe oxide to bind Si is exceeded at this Si level. The surface area increased from 65 to 352 m^2/g as the Si level in the system rose, thereby reflecting the mineralogy (as discussed below).

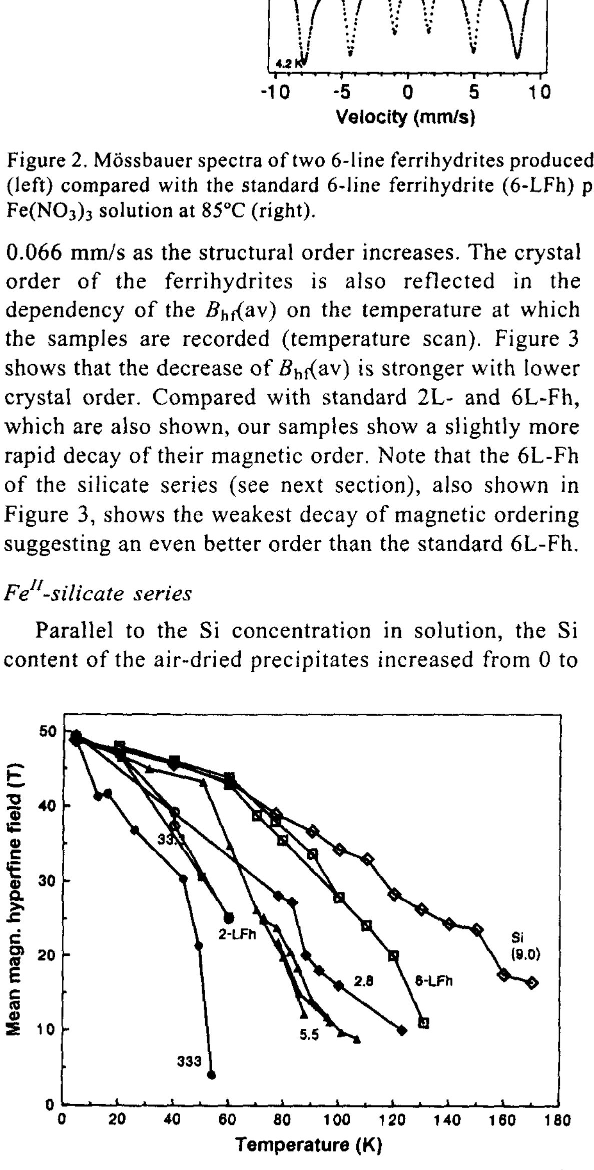

Figure 3. Temperature dependence of the magnetic hyperfine field for a range of ferrihydrites of various crystallinities produced by hydrolyzing 50 mL of a 0.1 M $Fe(NO_3)_3$ solution at a rate of 2.8, 5.5, 33.3 and 333 μmol OH min^{-1}. For comparison, a 6L-ferrihydrite (6L-Fh) produced by oxidizing an $FeCl_2$ solution containing 9 mmol L^{-1} Si (9.0) is also included.

The variation in mineralogy of the Fe^{II}-Si series was remarkably similar to those in the HR series: as the [Si] in solution decreased, a complete series from 2L- to 6L-ferrihydrite and then to lepidocrocite and goethite was formed (Figure 1, right). There are, however, some differences between the two series. The XRD peaks of the ferrihydrites are significantly sharper indicating a greater degree of crystallinity. Therefore, a higher magnetic ordering temperature can be expected. As seen from the temperature scan, this is indeed the case as long as the Si content is relatively low, *e.g.* in samples 75/9.0 (Figure 4) and 75/18.9. At higher Si contents, magnetic order is negatively affected by Si in the ferrihydrite leading to a significantly stronger breakdown of magnetic order (samples 33.8 and 73.0 in Figure 4). Incorporated Si also affects the B_{hf} at 4.2 K, whereas in the HR series, the hyperfine fields are at 48.8 T irrespective of their crystallinity and those in the Si series dropped significantly from 49.4 to 46.7 T (Table 2) as their Si content rose from 11.7 to 74.7 g/kg. Thus, the diamagnetic Si magnetically dilutes the oxide. An analogous observation was recently made for the DOM-ferrihydrite system (Schwertmann *et al.*, in prep.). Another difference between the two series lies in the ratio between goethite and lepidocrocite, the latter dominating, as might be expected, in the Fe^{II}-system.

Table 2. Properties of Fe oxides formed by oxidation of $FeCl_2$ in the presence of Si.

Si conc.	Surface area	Total Fe	Total Si	Minerals[1]			FWHH[2] of $Fh_{(112)}$	Hyperfine properties at 4.2 K			
				Fh	Lp	Gt		Ferrihydrite		Lepidocrocite	
								B_{hf}(av)	ΔE_Q	B_{hf}	ΔE_Q
μmol L^{-1}	m^2/g	g/kg	g/kg	%	%	%	°2θ	T	mm/s	T	mm/s
0	65	587	0	0	91	9	–	–	–	43.6	0.02
2.3	129	587	4.7	18	82	–	–	49.4	−0.084	43.3	.04
4.0	108	597	4.9	46	54	–	–	49.4	−0.164	45.6?	0.005
6.6	182	597	9.6	85[2]	15[2]	tr.	1.17	n.d.[3]	n.d.	n.d.	n.d.
9.0	179	591	11.7	89	11	–	1.04	49.3	−0.042	43.7	0.036
19	173	554	28.2	92	–	8	1.05	48.7	−0.041	–	–
29	270	497	48.4	100	0	–	1.88	48.2	−0.028	–	–
34	294	470	55.4	100	0	–	3.62	47.7	−0.028	–	–
73	352	419	74.7	100	0	–	5.77	46.7	−0.030	–	–

[1] by Mösbauer spectroscopy; [2] by XRD (Fh – ferrihydrite; Lp – lepidocrocite; Gt – goethite; full width at half height
[3] not determined

CONCLUSIONS

As found in natural surface environments, ferrihydrites with the full range of crystallinity between 2 and 6 XRD peaks can be produced easily either by varying the rate of supply of structural units to the growing crystal or by interfering with crystal growth through silicate anions. For the HR series this would mean that the rate of hydrolysis of Fe^{3+} determines the rate at which the building units are supplied to the growing crystal, a factor which may also vary widely in nature either by the supply rate of Fe and/or of the base. These building units for this process are thought to be small, partly hydrolyzed entities, such as $Fe(OH)^{2+}$ and its dimer $Fe_2(OH)_2^{4+}$. These units are probably attached to the surface of the growing crystal where they fully hydrolyze as they become part of the structure. The role which the rate of hydrolysis may play in affecting the size/order of the crystal may then be seen in the possibility for the building unit to attain an energetically more or less favorable position. This in turn will determine structural order: the faster the supply, the less perfect will be the final attachment to the surface and the more disordered will be the structure. The mechanism operating in the Fe^{II}-Si system may be different, although following the same principle. The tetrahedrally coordinated $Si(O,OH)_4$ unit, adsorbed at the surface, efficiently hinders the build-up of the framework of the $Fe(O,OH)_6$ octahedra as clearly suggested by the Mössbauer spectra even at 4.2 K (Figure 4). Therefore, at a constant rate of supply of growth units, as in our experiment, the crystal order will be lower, the higher the [Si] in solution. In conclusion, the factor responsible for crystal quality in the Fe^{III} system appears to be the supply rate of growth units whereas in the Fe^{II}-Si system it is the interference of a structure-building 'enemy'.

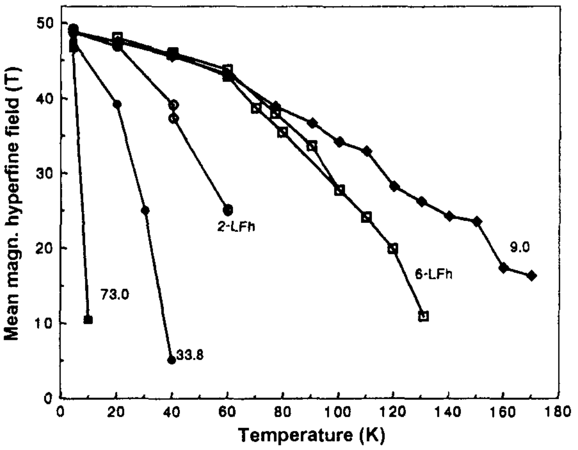

Figure 4. Temperature dependence of the magnetic hyperfine field for three ferrihydrites of various crystallinities produced by oxidizing an $FeCl_2$ solution containing 9.0, 33.8 and 73.0 mmol L^{-1} Si. The standard 2- and 6-line ferrihydrites are shown for comparison.

ACKNOWLEDGMENTS

We thank Prof F. Wagner for permission to produce Mössbauer spectra at the Fakultät für Physik in Garching, Prof H. Stanjek, Aachen, for advice, and him and Prof. J. Torrent, Cordoba, for critically reviewing the paper. The Deutsche Forschungsgemeinschaft is thanked for financial support (Schw.90-50).

REFERENCES

Carlson, L. and Schwertmann, U. (1981) Natural ferrihydrites in surface deposits from Finland and their association with silica. *Geochimimica et Cosmochimica Acta*, **45**, 421–429.

Carlson, L. and Schwertmann, U. (1990) The effect of CO_2 and oxidation rate on the formation of goethite versus lepidocrocite at pH 6 and 7. *Clay Minerals*, **25**, 65–71.

Chukhrov, F.V., Zvyagin, B.B., Ermilova, L.P. and Gorshkov, A.I. (1973a) New data on iron oxides in the weathering zone. *Proceedings of the International Clay Conference, Madrid (1972)*, 333–341.

Cornell, R.M. and Schwertmann, U. (2003) *The Iron Oxides*, 2nd edition. Wiley-VCH, Weinheim, Germany, 664 pp.

Drits, V.A., Sakharov, B.A., Salyn, A.L. and Manceau, A. (1993) Structural model for ferrihydrite. *Clay Minerals*, **28**, 185–207.

Dzombak, D.A. and Morel, F.M.M. (1990) *Surface*

Complexation Modeling. Hydrous Ferric Oxide. J. Wiley, New York, 393 pp.

Eggleton, R.A. and Fitzpatrick, R.W. (1988) New data and a revised structural model for ferrihydrite. *Clays and Clay Minerals*, **36**, 111–124.

Friedl, J. and Schwertmann, U. (1996) Aluminium influence on iron oxides: XVIII. The effect of Al substitution and crystal size on magnetic hyperfine fields of natural goethites. *Clay Minerals*, **31**, 455–464.

Jambor, J.L. and Dutrizac, J.E. (1998) Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. *Chemical Reviews*, **98**, 2549–2585.

Janney, D.E., Cowley, J.M. and Buseck P.R. (2000a) Transmission electron microscopy of synthetic 2- and 6-line ferrihydrite. *Clays and Clay Minerals*, **48**, 111–119.

Janney, D.E., Cowley, J.M. and Buseck P.R. (2000b) Structure of synthetic 2-line ferrihydrite by electron nanodiffraction, *American Mineralogist*, **85**, 1180–1187.

Kämpf, N. and Schwertmann, U. (1983) Goethite and hematite in a climosequence in Southern Brazil and their application in classification of kaolinitic soils. *Geoderma*, **29**, 27–39

Lewis, D.G. and Cardile, C.M. (1989) Hydrolysis of Fe(III) solution to hydrous iron oxides. *Australian Journal of Soil Research*, **27**, 103–115.

Murad, E. (1996) Magnetic properties of microcrystalline iron(III) oxides and related materials as reflected in their Mössbauer spectra. *Physics and Chemistry of Minerals*, **23**, 248–262

Murad, E. and Schwertmann, U. (1980) The Mössbauer spectrum of ferrihydrite and its relation to those of other iron oxides. *American Mineralogist*, **65**, 1044–1049

Murad, E., Bowen, L.H., Long, G.J. and Quin, T.G. (1988) The influence of crystallinity on the magnetic ordering in natural ferrihydrites. *Clay Minerals*, **23**, 161–173.

Murphy, P.J., Posner, A.M. and Quirk, J.P. (1976) Characterization of partially neutralized ferric nitrate solutions. *Journal of Colloid and Interface Science*, **56**, 270–283.

Schwertmann, U. and Cornell, R.M. (2000) *Iron Oxides in the Laboratory*, 2nd edition. VCH, Weinheim, Germany, 188 pp.

Schwertmann, U. and Taylor, R.T. (1979) Natural and synthetic poorly crystalline lepidocrocite. *Clay Minerals*, **14**, 285–293.

Stanjek, H. and Schwertmann, U. (1992) The influence of aluminum on iron oxides. Part XVI: Hydroxyl and aluminum substitution in synthetic hematites. *Clays and Clay Minerals*, **40**, 347–354.

Towe, K.M. and Bradley, W.F. (1967) Mineralogical constitution of colloidal "hydrous ferric oxides". *Journal of Colloid and Interface Science*, **24**, 384–392.

(Received 30 July 2003; revised 10 October 2003; Ms. 824; A.E. Helge Stanjek)