

Ferrihydrite–Humic Associations: Magnetic Hyperfine Interactions

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ABSTRACT

Humic–iron oxide associations are believed to exist in various surface environments, such as soils and surface waters, and may add substantially to the stability of organic matter under oxidizing surface conditions. However, a nondestructive, solid-state characterization of such associations is still lacking. In this paper synthetic coprecipitates between humic material (dissolved organic matter; DOM) obtained from a Podzol and synthetic ferrihydrite are examined using X-ray diffraction (XRD) patterns and Fe-specific Mössbauer spectra at temperatures between 4.2 K and room temperature. Lepidocrocite formed in the absence of DOM. However, DOM induced the formation of a four (XRD)-line ferrihydrite that contained 96 mg C/kg. In contrast to a pure four-line ferrihydrite, which was completely magnetically ordered at 4.2 K, the synthesized DOM–ferrihydrite was not fully ordered at 4.2 K and had a magnetic hyperfine field 1 to 2 T lower than the pure ferrihydrite. Such an effect was not observed when DOM was only surface-adsorbed. We conclude that organic components of the DOM coprecipitated with the ferrihydrite. Their interaction with the Fe atoms of the oxide prevents complete spin freezing at 4.2 K. Solid-state ^{13}C nuclear magnetic resonance (NMR) spectra suggested that O-alkyl C of the DOM was mainly responsible for the interaction with the Fe in the oxide.

STATISTICAL CORRELATIONS between the carbon and iron oxide content in surface environments, such as soils (Stucki et al., 1988; Kaiser et al., 1997; Kaiser and Guggenberger, 2000; Cornell and Schwertmann, 2003) and surface waters (Tipping, 1981), have suggested that humics are intimately associated to nanosized iron oxides based on an interaction between negatively charged humics and positively charged iron oxides. Unspecified interaction between humics and natural iron oxides was demonstrated by a modification of the oxides after removal of humics. Oxidation with HClO_4 of a goethite–humic composite from a Brazilian Oxisol drastically raised the Brunauer–Emmett–Teller (BET) N_2 surface area, P adsorption, and the zero point of charge of the goethite (Fontes et al., 1992). Similarly, on peroxidation, the specific surface area of a ferrihydrite–humics complex from a ditch in a high-moor peat containing 235 g/kg Fe and 24.7 g/kg C was doubled (from 163 to 323 m^2/g), the magnetic hyperfine field at 4.2 K as obtained from Mössbauer spectra increased from 46.5 to 47.7 T, and its quadrupole split at 292 and 4.2 K decreased from 0.793 to 0.706 mm/s. This was explained by a decrease of the site distortion of the octahedral Fe, possibly due to

partial removal of interacting organic molecules (Schwertmann and Murad, 1988). These latter results indicate that humics may not only be adsorbed to the surface but may also be coprecipitated with the iron oxides. This, in turn, may affect crystal order of metastable iron oxides and hinder their transformation into more stable forms, such as ferrihydrite to goethite (Schwertmann, 1966).

A different approach to specify the interaction between humic material and iron oxides consists of comparing laboratory preparations produced either by adsorption of DOM on or coprecipitation with synthetic iron oxides. Using a synthetic iron oxide mineral similar to those in natural environments would facilitate the description of any possible iron oxide–humic associates. The latter appears attractive in view of such a process in soils, especially in Podzols, in which both constituents are assumed to comigrate from the topsoil into the subsoil where they coprecipitate due to an increase in pH and/or in the Fe to C ratio. In contrast to Fe–humic complexes with comparatively low Fe to C ratios (e.g., Kodama et al., 1988), the characterization of synthetic iron oxide–humic associates with relatively high Fe to C ratios by nondestructive, solid-state methods is essentially lacking although interactions between humics and iron oxides are assumed to exist in many soils. The function of the iron oxides is, among others, being seen in their stabilizing effect on humic material.

^{57}Fe -Mössbauer spectroscopy allows one to characterize the chemical environment of the iron atom [for a comprehensive treatment see Murad and Cashion (2004)]. For example, a weak magnetic hyperfine sextet with a field of 47.3 T at 4.2 K was found for a humic–Fe compound with an Fe content of 15.4 g/kg (Kodama et al., 1988). We, thus, used ^{57}Fe Mössbauer spectroscopy at low temperatures to characterize the magnetic hyperfine interactions in a synthetic DOM–iron oxide coprecipitate. This technique supplies also specific information about the interaction of iron compounds with other phases and allows a distinction between Fe bound in oxides and nonoxidic compounds (Murad and Cashion, 2004). Whereas Fe(III) located in iron oxides (i.e., Fe in a framework of O and OH) orders magnetically, especially at lower temperatures, Fe diluted in silicates and other compounds does not. The spectra also permit a quantification of the different Fe forms. We, therefore, postulate that Mössbauer spectroscopy can distinguish between oxidic and nonoxidic Fe in the ferrihydrite–DOM coprecipitate.

In solid-state ^{13}C NMR spectroscopy, paramagnetic compounds such as iron oxides present an efficient relaxation pathway for organic C and protons in their close proximity. The relaxation can be so fast that after excitation of the spin system, the latter returns to its thermal equilibrium before acquisition of the signal has fin-

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Abbreviations: DOM, dissolved organic matter; NMR, nuclear magnetic resonance; XRD, X-ray diffraction.

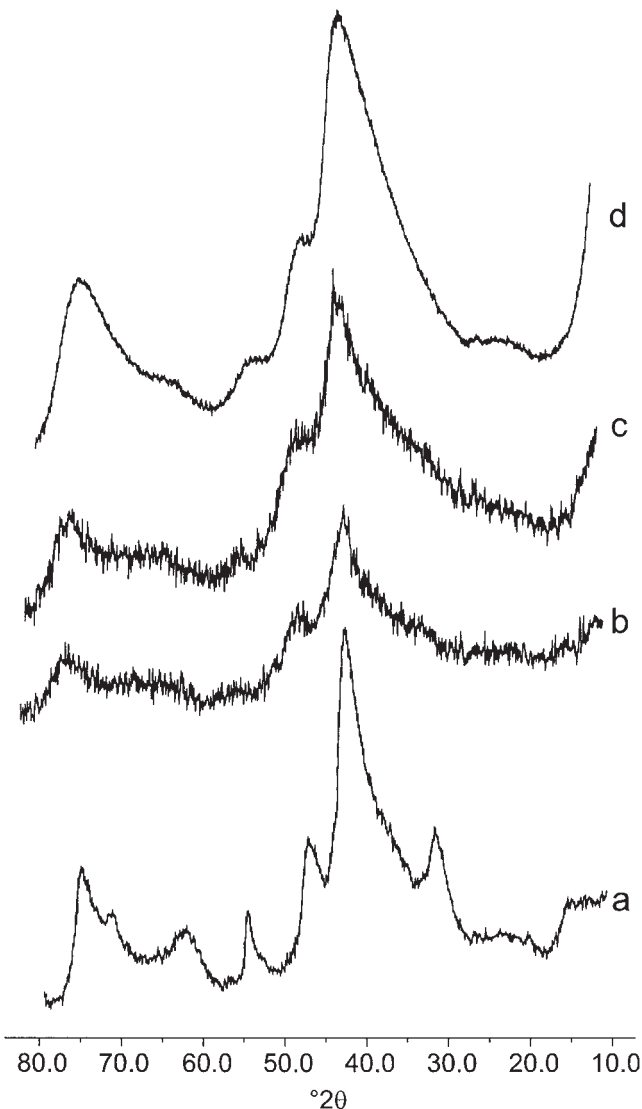


Fig. 1. X-ray diffraction patterns: (a) 79/05R, reference sample formed by rapid oxidation of a FeCl_2 solution at pH 5.5; (b) 79/05; (c) 79/07, same as 75/05R, but in the presence of dissolved organic matter (DOM); and (d) 74/2, for comparison, four-line ferrihydrite, precipitated by rapid hydrolysis of a $\text{Fe}(\text{NO}_3)_3$ solution at pH 7 (Schwertmann et al., 2004).

ished. Signal intensity loss and considerable line broadening, thus, have to be encountered. On the other hand, as a nondestructive technique it allows the structural characterization of the organic matter fraction of the bulk sample without any pretreatment and irrespective of its solubility.

The objectives of this study were to demonstrate the existence of a solid-state association between iron oxides and humics with the help of Mössbauer spectroscopy as a nondestructive method. Nuclear magnetic resonance spectroscopic analysis of the DOM before coprecipitation with Fe was used to obtain information about possible C functional groups involved in the reaction.

MATERIALS AND METHODS

Dissolved organic matter was extracted from a field-moist organic (Oh) horizon of a Podzol formed on gravely sand

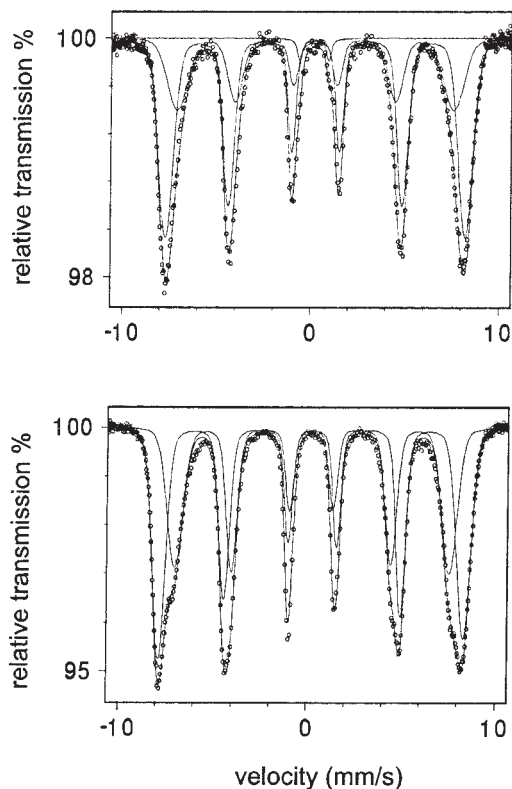


Fig. 2. Mössbauer spectra at 4.2 K: (top) sample prepared by rapid oxidation of a FeCl_2 solution at pH 5.5 in the presence of dissolved organic matter (DOM) and (bottom) reference sample without DOM.

(Tertiary Molasse) near Freising (Southern Bavaria; $11^\circ 35' \text{ E}$, $48^\circ 27' \text{ N}$). The samples were deep-frozen at -40°C after sampling and thawed shortly before use. After sieving at $<3.15 \text{ mm}$, 233 g were end-over-end shaken at room temperature with 0.7 L of distilled water for 16 h at 200 rpm. The extract was sieved at $<0.2 \text{ mm}$ and centrifuged for 1 h at 4000 rpm, and the solution was pressure-filtered at $<0.45 \mu\text{m}$. This solution contained 162.4 mg/L C (determined with the Shimadzu [Kyoto, Japan] TOC 5050A instrument), 0.74 mg/L Fe, and 1.4 mg/L Si (both determined by atomic absorption spectroscopy using a Solar 939 instrument; Unicam Ltd., Cambridge, UK) and had a pH of 3.65.

The chemical characteristics of the DOM samples were disclosed by solid-state ^{13}C NMR spectroscopy using a Bruker (Billerica, MA) DSX 200 spectrometer operated at a ^{13}C resonance frequency of 50.3 MHz, and using a commercial Bruker double-bearing probe with phase-stabilized zirconium dioxide rotors of 7-mm o.d. The cross-polarization magic-angle spinning (CPMAS) technique was applied at 6.8 kHz. A ramped ^1H -pulse was used during contact time of 1 ms to circumvent Hartmann–Hahn mismatches (Cook et al., 1996). After accumulation of 2000 single scans at a pulse delay of 400 ms, the spectrum was Fourier transformed with a line broadening of 50 Hz. The ^{13}C chemical shift scale is referenced to tetramethylsilane (=0 ppm) and was adjusted with glycine (=176.04 ppm) as an external standard. For quantification, the spectrum was divided into six chemical shift regions (Knicker and Lüdemann, 1995) and the regions were integrated using the instrument software.

Two DOM–iron oxide coprecipitates, labeled 79/05 and 79/07, were produced by oxidizing a solution consisting of 5 mL of 1 M FeCl_2 in 500 mL of a N_2 -purged DOM solution (11.08 mg/L) at pH 5.5 in an open vessel under stirring while the pH

Table 1. Mössbauer data of dissolved organic matter (DOM)–iron oxide coprecipitates and their reference samples.

Preparation	Sample	Temperature	ΔE_Q^\dagger	B_{hf}^\ddagger	Proportion	Assignment
			mm/s	T	%	
Fe(II) + DOM	79/05	RT§	0.70	–	100	ferrihydrite
		4.2 K	0.8Ff	–	9	Fe–DOM
		ditto	0.8Ff	39.1	91	ferrihydrite
Ditto	79/07	RT	0.80	–	100	ferrihydrite
		4.2 K	0.04	48.1	100	ferrihydrite
		ditto	0.04	48.1	100	ferrihydrite
Fe(II)	79/05 ref.	RT	0.74	–	81	ferrihydrite
		ditto	0.54	–	19	lepidocrocite
		4.2 K	0.05	50.4	83	ferrihydrite
		ditto	0.06	45.6	17	lepidocrocite
Fe(III) + DOM	81/1	RT	0.77	–	100	ferrihydrite
		4.2 K	–0.02	48.3	100	ferrihydrite
		ditto	–0.02	48.3	100	ferrihydrite
Fe(III)	81/1 ref.	RT	0.79	–	100	ferrihydrite
		4.2 K	–0.011	49.3	100	ferrihydrite

[†] Quadrupole split.

[‡] Magnetic hyperfine field.

[§] Room temperature.

was automatically kept constant with 0.3 M NaOH. A third coprecipitate (Sample 81) was synthesized by quickly raising the pH from 1.60 to 3.65 in 50 mL of a 0.1 M Fe(NO₃)₃ solution containing 7.515 mg C/L. The precipitates were separated by centrifugation, thoroughly washed with water, and dried at 40°C. Samples in which DOM was supposed to be surface-adsorbed were synthesized by shaking 200 mg of a freeze-dried six- and two-line ferrihydrite (six-line = six XRD peaks) four times (three times for 15 h and the fourth time for 70 h) with the same DOM solution. For comparison, four DOM-free samples were included: a six- and two-line ferrihydrite synthesized by standard procedures (Schwertmann and Cornell, 2000), and a two- and four-line ferrihydrite formed by rate-controlled hydrolysis of a Fe(NO₃)₃ solution (Samples 74/1 and 74/3) (Schwertmann and Friedl, 2005).

The coprecipitates were characterized by X-ray diffraction using CoK_α radiation at 40 kV and 40 mA on a Philips (Eindhoven, the Netherlands) vertical goniometer (PW 1050) fitted with a 1/2° divergence slit, 0.2-mm receiving slit, 1° scatter slit, and an AMR diffracted beam graphite monochromator. The samples were step scanned from 3 to 100° 2θ at 0.02° 2θ steps with a 5-s counting time per step. Mössbauer spectra were recorded at room temperature and 4.2 K using a velocity drive equipped with a ⁵⁷Co–Rh source in sinusoidal mode. To follow the breakdown of magnetic order, spectra were also taken while the temperatures were stepwise raised from 4.2 up to approximately 70 K. The spectra were fitted with sets of Gaussian distributions of Lorentzian-shaped lines for the magnetic sextets and quadrupole doublets (Friedl and Schwertmann, 1996). Surface area was measured by N₂ adsorption with a conventional volumetric apparatus using an Autosorb 1 surface area analyzer (Quantachrome Corporation, Boynton Beach, FL).

RESULTS AND DISCUSSION

The two DOM–ferrihydrite coprecipitates (79/05 and 79/07) contained 97 and 95 mg C/g, whereas in the adsorption experiment, two- and six-line ferrihydrite adsorbed only 3.3 and 24.2 mg C/g, respectively. This suggests that coprecipitation leads to a kind of mixed component rather than to surface-adsorbed humics only. The crystallinity of these compounds evolves from their XRD patterns (Fig. 1). Compared with the reference sample produced in the absence of DOM, which consisted of six-line ferrihydrite with some lepidocrocite, no lepidocrocite and a ferrihydrite with only four broad peaks were formed. This is to say that the conditions for crystallization are

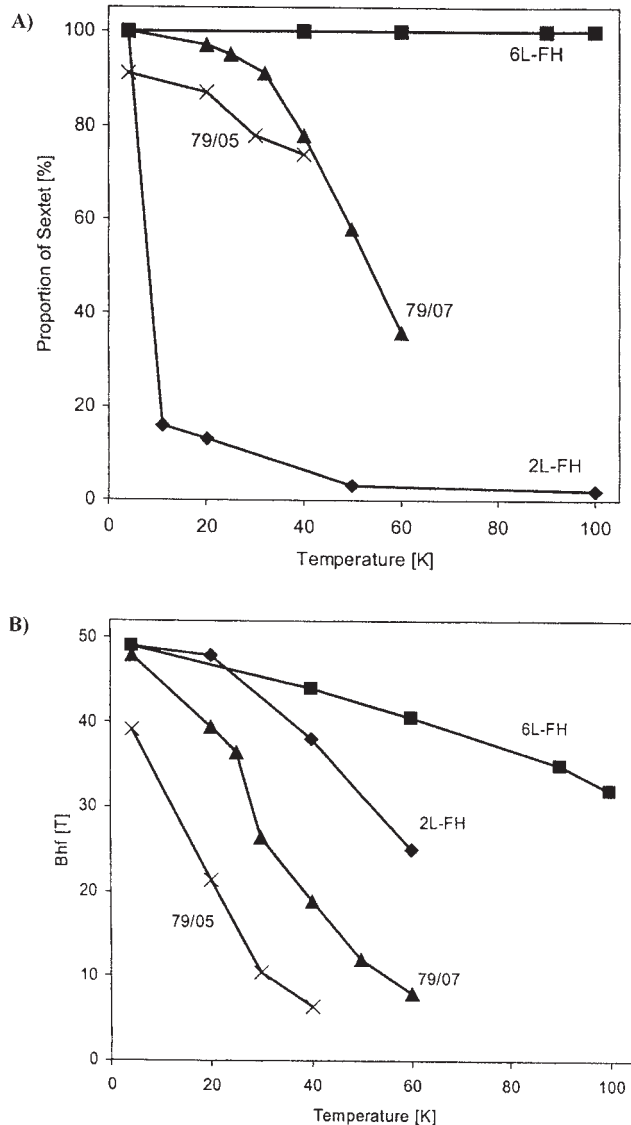


Fig. 3. Effect of temperature on the (A) sextet proportion and (B) the magnetic hyperfine field (B_{hf}) of dissolved organic matter (DOM)–iron oxides as compared with standard two- and six-line ferrihydrites.

significantly deteriorated by humic material. We recently showed (Schwertmann and Friedl, 2005) that the same effect can be produced by varying the rate of crystallization.

Surprisingly, the significantly lower particle size of the product formed when DOM was present is not reflected in a higher N_2 -specific surface area. On the contrary, its specific surface area is much lower ($65.8 \text{ m}^2/\text{g}$) than that of the blank ($265 \text{ m}^2/\text{g}$). We presume that strong aggregation of the nanoparticles in the DOM-ferrihydrite coprecipitate made a large part of the surface inaccessible to N_2 adsorption.

Mössbauer spectra at 4.2 K support the above conclusions and provide further information. The spectrum of the blank (Fig. 2A) consists of a hyperfine sextet, which indicates complete magnetic ordering at this temperature. Because of its asymmetric dips it had to be fitted with two sextets whose magnetic hyperfine field (B_{hf}) values of 50.4 and 45.6 T are those of ferrihydrite and lepidocrocite, respectively (intensity ratio of approxi-

mately 81:19; Table 1). This is in agreement with the results obtained from XRD.

In contrast, the spectrum of the DOM-ferrihydrite (Fig. 2B) shows only one sextet whose asymmetric shape toward smaller B_{hf} values shows a distribution of hyperfine fields peaking at 48 T as the most frequent B_{hf} . This value indicates ferrihydrite rather than lepidocrocite and its asymmetry can be interpreted as distribution of particle sizes and/or crystallinities. Thus, results from Mössbauer spectra are in agreement with those from XRD with respect to small particle size and/or poor crystallinity.

The Mössbauer spectrum provides, however, additional information about the properties of the DOM-ferrihydrite that cannot be extracted from XRD patterns (Fig. 3). First, the sextet of the DOM-ferrihydrite comprises only 90% of the Fe in the sample and its B_{hf} was approximately 2 T lower than that of pure ferrihydrite. Second, the remaining 10% of the Fe appears in the spectrum as a doublet, which means that it is not ordered magnetically even at 4.2 K. It allows one to

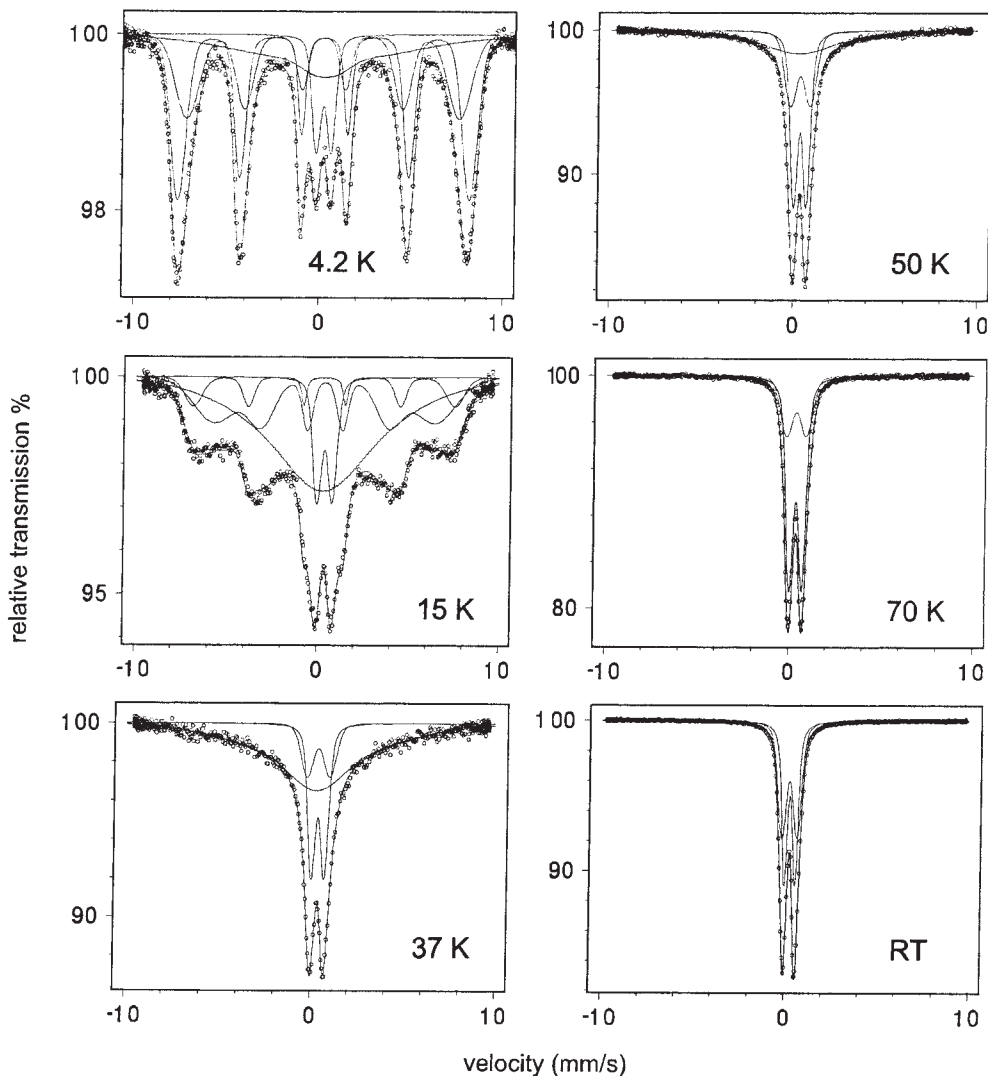


Fig. 4. Effect of temperature on the Mössbauer spectra of a dissolved organic matter (DOM)-iron oxide (79/05) measured between 4.2 and 70 K, plus room temperature (RT).

attribute this Fe fraction to nonoxidic Fe, most likely an Fe–DOM complex. To the best of our knowledge, this would then be the first identification of such a complex by a nondestructive, solid-state method. A similar result was obtained with a precipitate from a Fe(III) solution in the presence of DOM (Sample 81 in Table 1): again the two-line ferrihydrite formed had a B_{hf} of only 48.3 T (Table 1). This is to say that only 91% of the Fe in Sample 79/05 appeared as a sextet whereas the remaining 9% appear in the doublet rather than in the sextet.

At this point we conclude that on oxidizing Fe(II) in the presence of DOM, the organic material

- (i) suppressed the formation of lepidocrocite in favor of ferrihydrite,
- (ii) lowered the B_{hf} of the ferrihydrite, and
- (iii) in one case, induced a DOM–Fe complex that is not magnetically ordered even at 4.2 K.

The complex engaged approximately 10% of the Fe of the ferrihydrite in a way that hinders magnetic order even at very low temperature and means that it is not

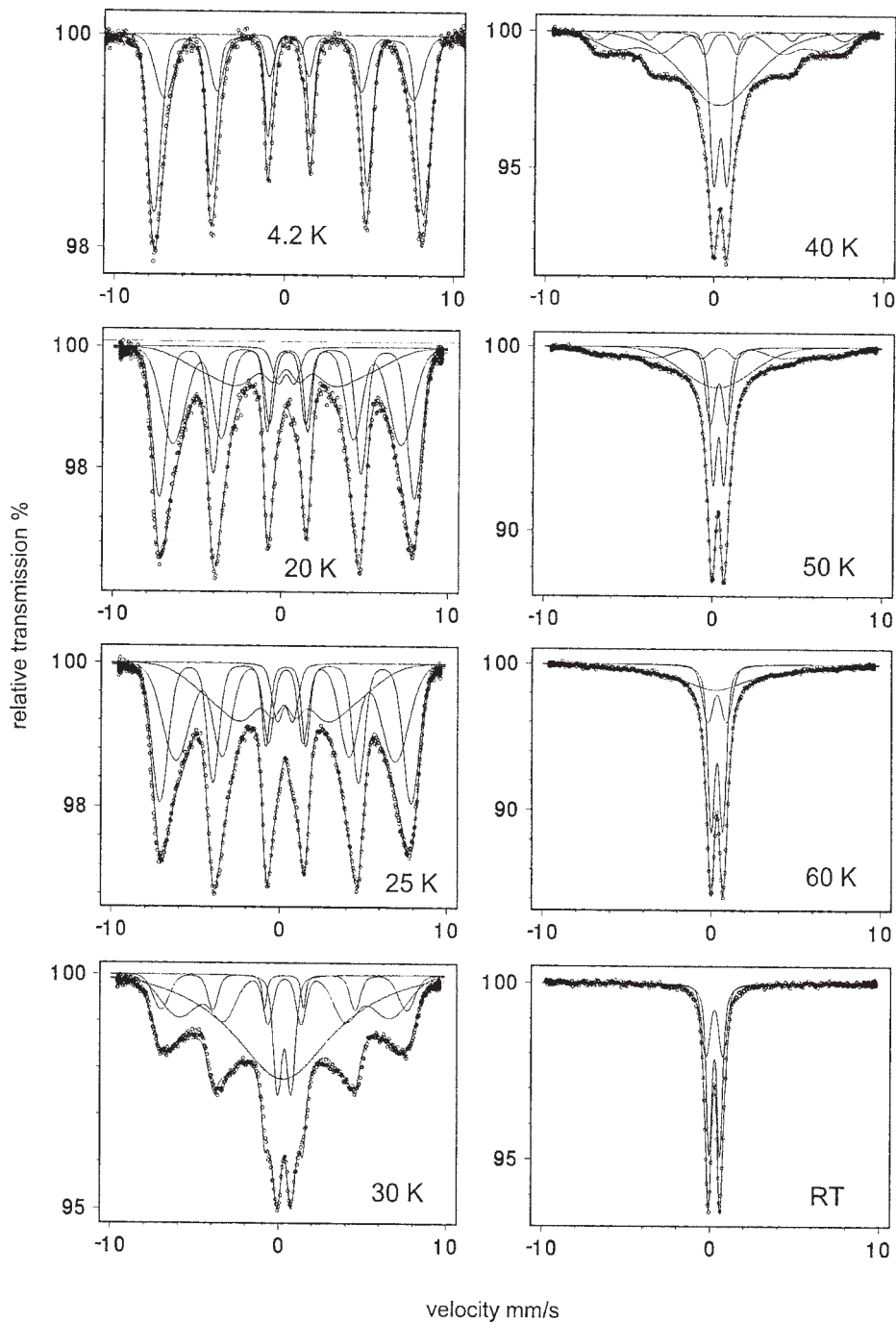


Fig. 5. Effect of temperature on the Mössbauer spectra of a dissolved organic matter (DOM)–iron oxide (79/07) measured between 4.2 K and room temperature (RT).

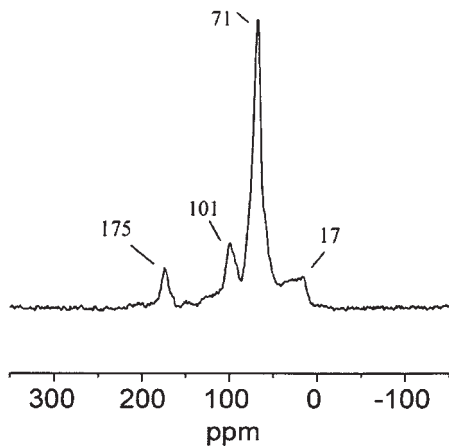


Fig. 6. Solid-state ^{13}C nuclear magnetic resonance (NMR) spectrum of the dissolved organic matter (DOM).

magnetically ordered even at 4.2 K, whereas Sample 79/07 is completely ordered (Fig. 3A). In other words, Sample 79/05 is more affected by DOM than Sample 79/07. Dissolved Si may also interfere with crystallization but the Si concentration in the DOM extract of only 1.4 mg/L is considered too low to have this effect (Schwertmann et al., 2004).

Further information about the structural order was extracted from the temperature-dependent Mössbauer spectra taken between 4.2 and 100 K (Fig. 4 and 5) (temperature scans). The temperature dependence of magnetic ordering provides information on structural order and impurities in the structure. In principle, poorly ordered or impure iron oxides and those containing diamagnetic compounds, such as Al, lose magnetic order with increasing temperature more quickly than pure and well crystalline ones.

As shown in Fig. 3, both the proportion of the sextet (Fig. 3A) and its average B_{hf} (Fig. 3B) decreased as the temperature increased. Also, the dips became broader and more asymmetric toward smaller hyperfine fields. The spectra could only be fitted reasonably well with three sextets whose B_{hf} values are expressed as weighted averages. With respect to the sextet proportion in the spectra (Fig. 3A), the two DOM-iron oxides are placed between the standard two- and six-line ferrihydrite in agreement with their intermediate crystallinity (Fig. 1). The B_{hf} (Fig. 3B), especially that of Sample 79/05, decreased much more rapidly with increasing temperature than even the most poorly ordered (two-line) ferrihydrite. This demonstrates that the effect of small amounts of diamagnetic material dispersed within the iron oxide has a remarkable effect on magnetic ordering.

We, therefore, conclude that coprecipitation with DOM modifies the hyperfine magnetic properties of iron oxides by local and long-range interaction. This results from Mössbauer spectra at 4.2 K. Approximately 10% of the Fe are not magnetically ordered and the magnetic hyperfine field has dropped by 2 to 3 T. It indicates that humics induce additional disorder in the ferrihydrite and that some of its Fe forms C–O–Fe bonds with the DOM throughout the sample. Such bonds may perturb the ligand shell of the Fe in the oxide and hinder its spin

freezing even at 4.2 K. In contrast to coprecipitation, adsorption of DOM by equilibrating two- and six-line ferrihydrite did not have such an interfering effect: the Mössbauer spectrum at 60 K showed a fully ordered sample (100% sextet). Since the coprecipitate had an XRD pattern very similar to that of a DOM-free four-line ferrihydrite (Sample 79/05), it is obvious that XRD does not recognize the structural interference by DOM in such a rather poorly ordered phase.

Our results show that organic compounds of the DOM are coprecipitated with Fe, thereby interacting markedly with the oxide throughout the solid phase. By this interaction, small proportions of the Fe may even be transferred from the oxide into a separate Fe–DOM complex as seen from the doublet comprising approximately 10% of the total absorption of the Mössbauer spectrum taken at 4.2 K.

The nature of the functional groups of the DOM that are involved in the interaction with Fe may be revealed by NMR spectroscopy (Fig. 6). The total aromatic C content (160 to 110 ppm) of the DOM comprises <6% and the O-aryl C does not exceed 1%. This proportion certainly cannot account for the observed coprecipitation. A clear signal is observed in the carboxyl–carbonyl–amide C region (220 to 160 ppm) accounting for 7% of the total C content. It peaks at 175 ppm and is typical for esters, indicating that free carboxyl C groups are not present to a large extent. Because the ratio of alkyl C (45 to 0 ppm) to carboxyl–carbonyl–amide C (220 to 160 ppm) is <1.7%, it can be assumed that the esters are mostly formed by short-chain acids. The clear signal at 17 ppm, attributable to terminal methyl C groups, confirms this assignment. The resonance line in the region between 60 and 45 ppm is indicative for methoxyl C and N-alkyl C (7–8%). The latter derive most likely from amino sugars or peptide structures, the amino group of which may also participate in the interaction between DOM and iron oxides. The most tentative involved functional groups, however, are O-alkyl C groups. Their resonance lines dominate the spectra with 65 to 75% of the total ^{13}C intensity. The peaks at 71 and 101 ppm assign them to carbohydrates, in which their C2, C3, C4, and C5 contribute to the region between 60 and 90 ppm. The intensity between 110 and 90 ppm originates from their anomeric C. Calculating the ratio (4.4) of those two regions indicates that mostly hemicellulosic material is present.

It appears that carbohydrates play a major role for the interaction of DOM with Fe. This conclusion is supported by former studies correlating the iron oxide content of 42 A horizons with the content of O-alkyl C as determined by solid-state ^{13}C NMR spectroscopy (Spielvogel et al., 2003). Examining the influence of paramagnetic Fe on solid-state CPMAS ^{13}C NMR spectra of sewage sludge, Pfeiffer et al. (1984) observed the strongest peak depression caused by interactions with the paramagnetic material for the O-alkyl C region, whereas the O-aryl C region remained almost unaffected. A possible explanation may be that the signal of O-aryl C derived mostly from aryl ethers, which offered no direct adsorption sites for paramagnetic Fe. In contrast, the OH groups

of carbohydrate can bind Fe(III) efficiently and consequently the respective ^{13}C NMR signals will be reduced.

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