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The Mössbauer spectrum of ferrihydrite and its relations to those of other iron oxides

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Abstract

The superparamagnetic Mössbauer spectra observed for ferrihydrite at room temperature are complex, and require fitting with at least two Lorentzian doublets to properly delineate the experimental data. Characteristic for such fits are a low (0.54 $mm \cdot s^{-1}$) and high (0.90 $mm \cdot s^{-1}$) quadrupole splitting. At 4K the Mössbauer spectrum of this mineral shows magnetic hyperfine splitting with a wide distribution of hyperfine fields, and a maximum absorption near 500 kOe.

Similar spectra are also shown by other iron oxides, especially hematite, of extremely small particle size (<100Å). This emphasizes basic structural relationships between the different iron oxides, but limits the applicability of Mössbauer spectroscopy as an analytical tool in this particle size range.

Introduction

Ferrihydrite is a naturally occurring iron oxide of bulk composition $5Fe_2O_3 \cdot 9H_2O$. Two different formulae proposed for ferrihydrite are $Fe_5HO_8 \cdot 4H_2O$ (Towe and Bradley, 1967) and $Fe_5(O_4H_3)_3$ by Chukhrov *et al.* (1972). From infrared absorption spectra Russell (1979) suggested OH to be an essential part of the structure and arrived at the formula $Fe_2O_3 \cdot 2FeOOH \cdot 2.6H_2O$.

Ferrihydrite is usually identified by X-ray diffraction which, however, is not very sensitive because this mineral yields very broad lines and often incomplete patterns due to small particle size (<100Å) and/or poor structural order. High solubility in ammonium oxalate can give an indication of the presence of ferrihydrite in natural samples (Schwertmann, 1964; 1979).

No information on the Mössbauer spectrum of this mineral from soils or sediments has been published to date. On the other hand, some earlier data on "amorphous iron oxide gels" may, in fact, refer to ferrihydrite. The Mössbauer spectrum of ferrihydrite may also be related to that of the iron core of the protein ferritin, to which it appears to be structurally similar (Harrison and Hoy, 1973).

In this study the Mössbauer spectra of synthetic and natural ferrihydrites are described and compared to published and our own (mostly unpublished) data on the other common iron oxide minerals.

Sample description

Of the synthetic samples studied, 13/0 was prepared by neutralizing a 0.5M $Fe(NO_3)_3$ solution with NH_4OH to a pH of 7.5, washing free of electrolyte, and freeze-drying. Sample DLF5 was prepared by hydrolyzing a 0.06M $Fe(NO_3)_3$ solution at 85°C, dialyzing the sol against distilled water, and freeze-drying (Towe and Bradley, 1967). Sample PT79 was prepared by passing O_2 through a 0.0125M $FeCl_2$ solution in the presence of 50 ppm SiO_2 (to suppress lepidocrocite formation) at pH 7.

The natural samples 2, 40A, 31, N162, and N196 were formed by rapid oxidation of ferriferous waters, resulting in heavy ochreous precipitates. The first three samples are from various localities in Finland (Carlson and Schwertmann, unpublished manuscript). N162 is from the vicinity of Hannover in N. Germany (Schwertmann and Fischer, 1973), and N196 is from the type locality in Kazakhstan, USSR (Chukhrov *et al.*, 1972).

X-ray diffraction shows these samples to cover a range of ferrihydrite crystallinity from a fully developed six-line pattern (31, N162, PT79, DLF5) to a very poorly ordered material which shows only the two *hk* lines at 2.5 and 1.5Å (2, 13/0). The six-line pattern is that of a well developed ferrihydrite; the two-line pattern corresponds to the most poorly ordered material, which consists only of planar arrangements of $Fe(O,OH,OH_2)_6$ octahedra without

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any stacking perpendicular to that plane. The two lines correspond to the main Fe–Fe distances of 2.52 and 1.45Å within this structure (Feitknecht *et al.*, 1973). This material can be considered to have the most primitive arrangement of $Fe(O,OH,OH_2)_6$ octahedra, and may be a precursor of numerous other iron oxides. In nature it was found to occur in close association with ferrihydrite, feroxyhite, and other iron oxides (Carlson and Schwertmann, unpublished manuscript).

Ratios of oxalate (Schwertmann, 1964) to dithionite soluble iron (Mehra and Jackson, 1960) were over 0.9 in all samples except PT79 (0.56) and DLF5 (0.45), indicating ferrihydrite to constitute at least the dominant part of the total iron oxides.

Experimental methods

Mössbauer spectra were taken using a $^{57}Co/Rh$ source mounted on a loudspeaker-type drive system. Spectra were run at room temperature and after cooling both source and absorber to about 130 and 4K in a cryostat. Absorbers for the room-temperature spectra consisted of 11 mg sample mixed with 34 mg sugar (to improve mechanical stability), spread uniformly over an area of 2 cm^2 in a plexiglas holder. At lower temperatures 40 mg of undiluted sample were used. The transmitted radiation was registered with a

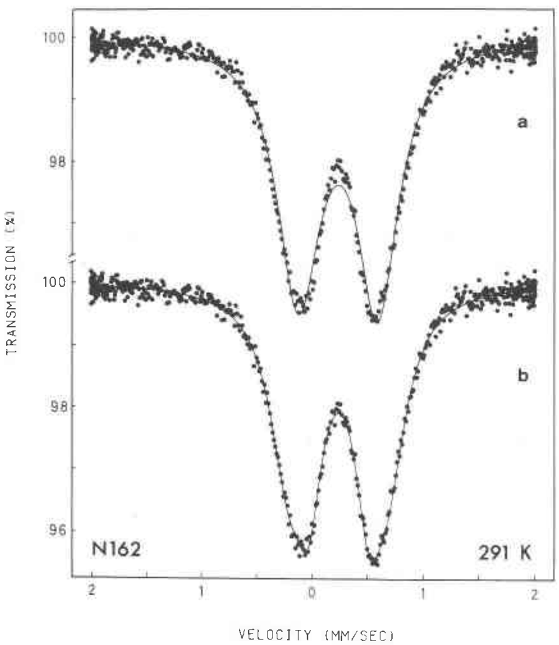

Fig. 1. Mössbauer spectrum of natural ferrihydrite N162 at room temperature, fitted with (a) one Lorentzian doublet (χ^2 = 1.41), (b) two Lorentzian doublets (χ^2 = 0.89).

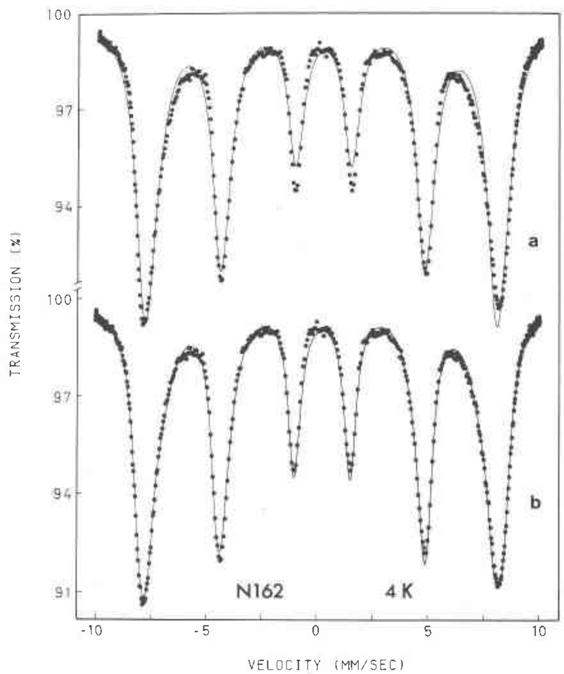

Fig. 2. Mössbauer spectrum of natural ferrihydrite N162 at 4K, fitted with (a) one sextet (χ^2 = 14.0), (b) three sextets (χ^2 = 3.4).

proportional counter and fed into a 1024-channel analyzer. Counting proceeded until sufficiently good statistics, visually monitored with an oscilloscope, had been attained. The data were folded, plotted, and Lorentzian curve fits carried out by a computer procedure. Pure metallic iron served as a standard for velocity calibration and as reference material for isomer shifts.

Results

At room temperature and 130K the Mössbauer spectra showed only a paramagnetic doublet. At 4K all spectra were completely split magnetically.

Fitting one doublet to the room temperature and 130K spectra, and one sextet to the spectra taken at 4 K resulted in only moderate coincidence with the actual line shapes (Figs. 1a, 2a). Line widths computed from such fits were exceedingly high, averaging about 0.45 $mm \cdot s^{-1}$ at room temperature, 0.53 $mm \cdot s^{-1}$ at 130K, and over 1 $mm \cdot s^{-1}$ at 4K.

Fitting two doublets to the room-temperature spectra lowered the χ^2 values (normalized by dividing χ^2 by the number of channels minus fit parameters) from an average of 1.45 to 0.95. The two doublets differ noticeably in their quadrupole splittings (0.89 and 0.54 $mm \cdot s^{-1}$) and line widths (0.45 and 0.31 $mm \cdot s^{-1}$), whereas the isomer shifts (0.34 and

0.35 mm · s^{-1}) vary significantly neither between the two doublets, nor from sample to sample.

The magnetically split spectra had to be fitted with three sextets to obtain acceptable χ^2 values. These fits, constrained to have identical isomer shifts for all sextets, showed the samples to have low and only slightly different quadrupole splittings, but a wide spread of magnetic hyperfine fields between about 445 and 510 kOe. A more realistic analysis was attained by fitting these spectra with series of up to twelve sextets, constrained to have identical line widths, isomer shifts, and quadrupole splittings. Such fits showed the ferrihydrites to possess distributions of magnetic hyperfine fields that are slightly skewed towards lower values, with maxima somewhat below 500 kOe (Fig. 3).

Parameters resulting from the individual fits of the room temperature and 4K spectra are given in Table 1. The spectra registered at 130K resemble those at room temperature (except for increased line widths), and are therefore not included in the table.

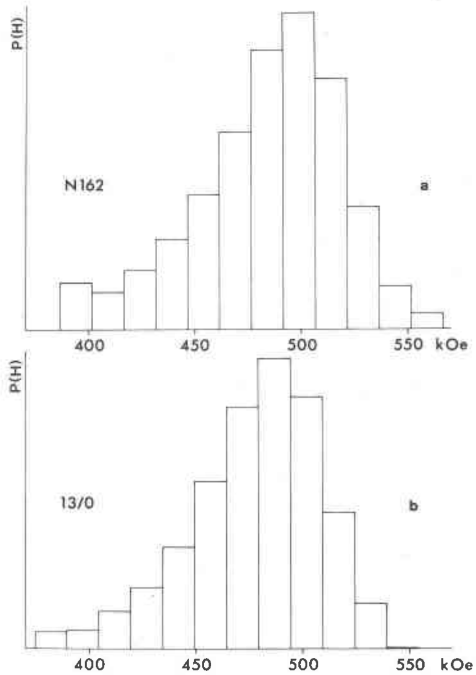

Fig. 3. Distributions of magnetic hyperfine fields at 4K for (a) natural ferrihydrite N162, and (b) synthetic ferrihydrite 13/0.

Discussion

Comparison with published values for "amorphous iron oxide gels" and ferritin

Most published quadrupole splittings of room-temperature "amorphous iron oxide" spectra (Table 2) are lower than those obtained here for a one-doublet fit of ferrihydrite (0.75 mm · s^{-1}), but higher than those of the other common iron oxides of not too small particle size (*ca.* 0.55 mm · s^{-1}). Only one of these previously described samples, which had been precipitated from an $Fe(NO_3)_3$ solution (Giessen, 1966) was, however, shown by X-ray diffraction to consist of ferrihydrite. Potvin and Greenblatt (1969) suggested that akaganéite may form when such gels are precipitated from $FeCl_3$ solutions. Impurities that gave a magnetically split spectrum at 70 K—the hyperfine field of 480 kOe indicates goethite—were observed in another case (Brady *et al.*, 1967).

Only two of the synthetic samples studied here contained significant amounts of iron oxides other than ferrihydrite. These samples (PT79, which contained some feroxyhite and lepidocrocite, and DLF5, which contained lepidocrocite and goethite), which must therefore be excluded from the calculation of average parameters, had the lowest quadrupole splittings of all.

The quadrupole splitting of 0.72 mm · s^{-1}, observed at room temperature for a natural ferric gel—possibly ferrihydrite—precipitated near freshwater springs (Coey and Readman, 1973) agrees well with our values (Table 1).

The iron-storage protein ferritin has been shown to consist of micelles of "hydrated ferric oxide" about 40–70Å in diameter, surrounded by protein shells. The X-ray and electron diffraction data are identical to those of ferrihydrite (Towe and Bradley, 1967). Correspondingly, the Mössbauer spectrum of ferritin (Blaise *et al.*, 1965; Fischbach *et al.*, 1971; Williams *et al.*, 1978) closely resembles that of ferrihydrite as described here.

Our results

Adequately good delineations of the experimental data were obtained when the room-temperature spectra were fitted with two doublets and the 4K spectra with three sextets (Figs. 1b, 2b). The different parameters resulting from these fits (Table 1) can be used to characterize the samples. They should, however, not be taken as proof for the existence of discretely different iron sites in the ferrihydrite structure. The hyperfine field distributions of the magnetically split spectra (Fig. 3) rather indicate continuous variations of parameters, and therefore of environments of the iron nuclei.

Room-temperature spectra. Our unpublished studies have shown the quadrupole splittings of super-

Table 1. Mössbauer parameters of ferrihydrite

Sample	N/S*	T(K)	δ(Fe)	ΔE_Q	W	H_i
31	N	291	*0.35(1)*	*0.71(1)*	*0.45(1)*	-
			0.35(1)	0.85(3)	0.41(1)	-
			0.36(1)	0.51(2)	0.29(2)	-
N162	N	291	*0.35(1)*	*0.71(1)*	*0.45(1)*	-
			0.34(1)	0.89(2)	0.42(1)	-
			0.35(1)	0.54(1)	0.31(1)	-
		4	*0.32(1)*	*0.05(1)*	*1.19(2)*	*492(1)*
				0.02(1)	0.74(3)	508(1)
			0.33(1)	0.08(1)	0.90(4)	484(1)
				0.03(2)	1.40(7)	444(3)
40A	N	292	*0.35(1)*	*0.78(1)*	*0.46(1)*	-
			0.35(1)	0.98(2)	0.39(1)	-
			0.35(1)	0.59(1)	0.32(1)	-
N196	N	291	*0.35(1)*	*0.78(1)*	*0.52(1)*	-
			0.34(1)	0.88(2)	0.53(1)	-
			0.35(1)	0.55(1)	0.27(5)	-
2	N	291	*0.35(1)*	*0.83(1)*	*0.52(1)*	-
			0.35(1)	0.90(2)	0.50(1)	-
			0.36(1)	0.52(1)	0.24(5)	-
PT79**	S	290	*0.34(1)*	*0.69(1)*	*0.53(1)*	-
			0.34(1)	0.86(2)	0.53(1)	-
			0.35(1)	0.51(1)	0.34(1)	-
DLF5**	S	292	*0.35(1)*	*0.64(1)*	*0.42(1)*	-
			0.33(1)	0.86(1)	0.39(1)	-
			0.35(1)	0.52(1)	0.32(1)	-
13/0	S	291	*0.34(1)*	*0.71(1)*	*0.46(1)*	-
			0.33(1)	0.87(2)	0.43(1)	-
			0.34(1)	0.54(2)	0.34(2)	-
		4	*0.34(1)*	*0.02(1)*	*1.05(2)*	*484(1)*
				-0.01(1)	0.56(3)	505(1)
			0.34(1)	0.02(1)	0.72(3)	482(1)
				0.06(1)	0.90(4)	452(2)

* Natural/synthetic sample.

** Contains noticeable amounts of other iron oxides, as determined by XRD.

Italicized values: one doublet fit (room temperature) and one sextet fit (4K), respectively.

Isomer shifts (δ), quadrupole splittings (ΔE_Q) and widths (W) given in $mm \cdot s^{-1}$, magnetic hyperfine fields in kOe

paramagnetic goethite and lepidocrocite (*ca.* 0.52–0.55 $mm \cdot s^{-1}$), minerals which are often associated with ferrihydrite in nature, to be usually lower than that obtained for a one-doublet fit of ferrihydrite (0.75 $mm \cdot s^{-1}$). Goethites of very poor crystallinity, however, were found to have higher quadrupole splittings of up to 0.63 $mm \cdot s^{-1}$. The Mössbauer spectra of such goethites should—like those of ferrihydrite—also be fitted with two doublets. Parameters of such a fit are similar isomer shifts averaging 0.35 $mm \cdot s^{-1}$, but different quadrupole splittings of 0.50 and 0.77 $mm \cdot s^{-1}$, and rather wide (FWHM 0.45 $mm \cdot s^{-1}$) outer lines.

In synthetic microcrystalline hematite decreasing particle size results in lattice expansion, as though the crystals were subjected to a "negative pressure" (Schroeer and Nininger, 1967). Decreasing pressure, however, causes the quadrupole splitting of this mineral to increase, whereas the isomer shift remains essentially unchanged (Vaughan and Drickamer, 1967). Refined analyses showed that the room-temperature Mössbauer spectra of small particles (≤70Å) of hematite can be fitted with two partly overlapping doublets that have different quadrupole splittings of 0.52 and 0.90 $mm \cdot s^{-1}$ (Kraan, 1973). These components were considered to result from well-ordered inner and poorly-ordered surface regions of the particles, respectively.

These observations correlate very well with the observed Mössbauer spectrum of ferrihydrite, which has quadrupole splittings that are practically identical to those given by Kraan (1973) for ultrafine hematite. Note in this connection that the structure of ferrihydrite may be compared to that of a disordered hematite (Towe and Bradley, 1967).

4K spectra. The magnetically split spectra shown by ferrihydrite at 4K differ from those usually observed for the other iron oxides at this temperature. Our mostly unpublished studies show that the hyperfine fields of well crystallized hematite (540 kOe) and feroxyhite (529 kOe; Carlson and Schwertmann, 1980) are distinctly higher, and that of lepidocrocite (455 kOe) is lower than the maximum of the hyperfine field distribution of ferrihydrite (*ca.* 500 kOe, see Fig. 3). The hyperfine field of goethite (505 kOe) approaches that maximum more closely, especially when lowered by aluminum substitution, but both goethite and hematite have quadrupole splittings that differ from that of ferrihydrite (0.24 and −0.41 *vs.* 0.03 $mm \cdot s^{-1}$). The Mössbauer spectrum of akaganéite comprises at least three superimposed sextets

Table 2. Mössbauer parameters of "amorphous iron oxide gels"

Author(s)	N/S*	T(K)	δ(Fe)	ΔE_Q	H_i
Giessen (1967)	S	300	0.36	0.62	-
Brady *et al.* (1968)	S	298	0.39	0.67	-
		5			455
Mathalone *et al.* (1970)	S	29x	0.33	0.65	-
		5	0.40	-	480
Coey & Readman (1973)	N	296	0.35	0.72	-
		77	0.47	0.81	-
		4	0.48	0.03	458
Loseva & Murashko (1973)	S	29x	0.32	0.62	-
Kauffman & Hazel (1975)	S	300	0.37	0.63	-
Saraswat *et al.* (1977)	S	300	0.32	0.54	-
		77	0.43	0.68	-
Okamoto & Sekizawa (1979)	S	29x		0.60	-
		4	0.5	∿ 0	494-508

* Natural/synthetic sample.

that have similar hyperfine fields between 473 and 486 kOe, but different quadrupole splittings of 0.90, 0.30, and −0.05 mm · s^{-1} (Murad, 1979).

The (poorly ordered) surface regions of small hematite particles were found to have a reduced hyperfine field (Kraan, 1973). This was considered to be the result of decreasing mutual interactions of surface ions with decreasing particle size. The particle sizes at which such effects become noticeable (70–40Å) are quite comparable to those usually observed for ferrihydrite. The hyperfine field distributions shown by this mineral are probably the outcome of particle size distributions.

Conclusions

One-doublet and one-sextet fits of room temperature and 4K Mössbauer spectra of ferrihydrite can be used to characterize this mineral. Typical parameters of such fits are a high quadrupole splitting of 0.75 mm · s^{-1} at room temperature, and a hyperfine field of about 490 kOe at 4K.

Physically sound fits require the room temperature spectra of ferrihydrite to be fitted with at least two superparamagnetic doublets of similar isomer shifts but different quadrupole splittings. At 4K hyperfine splitting with a distribution of magnetic hyperfine fields is observed. Both effects are also shown by other iron oxides of extremely small particle size, for example hematite. It thus appears that—in the microcrystal range—as particle sizes decrease, the individual characteristics of the different iron oxides gradually disappear, until finally only fundamental structural elements of short-range order common to all, *i.e.* Fe^{3+} surrounded by six O, OH, and/or OH_2, remain. This is in agreement with the conclusions from X-ray diffraction.

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