

## Iron oxide mineralogy of some deep-sea ferromanganese crusts

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### ABSTRACT

Three ferromanganese crusts from the Central Pacific that contain between 15 and 20 wt% Fe<sup>3+</sup> were studied by X-ray diffraction and Mössbauer spectroscopy. The poor crystallinity of the Fe-bearing minerals prevented their unequivocal identification by X-ray diffraction. The moderately highly distorted site symmetry of the Fe atoms deduced from Mössbauer spectra taken in the paramagnetic state and extremely low magnetic hyperfine fields at 4.2 K indicate most of the Fe to be bound in a ferrihydrite-like phase that is intimately intergrown with the Mn oxides. Selective removal of manganese oxides with hydroxylamine chloride affects the iron oxides in these crusts and therefore cannot be recommended as a technique for iron oxide enrichment.

### INTRODUCTION

Deep-sea ferromanganese crusts and nodules have attracted considerable interest because of their potential value as cobalt and nickel ores. Previous work on such materials has consequently focused primarily on the concentrations of these metals and the growth rates. Some work has also been done on the mineralogy of the manganese oxides, which are considered to be the main seat of the heavy metals (see Burns and Burns, 1979).

Although the Fe concentration in marine ferromanganese deposits is usually about the same as that of Mn, only a few papers have been concerned with the Fe-containing minerals (e.g., Ostwald, 1984). Difficulties in their identification arise mainly from the poor crystallinity of the iron oxides (Giovanoli and Bürki, 1975; Halbach et al., 1982), which may be a result of interference by manganese oxides or other agents that impede crystal growth.

Using selected-area electron diffraction (SAED), Chukhrov et al. (1976) identified a previously unknown iron oxide with the formula FeOOH in some nodules from the Pacific Ocean and the Baltic, White, and Kara Seas. This phase was later recognized as a new mineral with the name ferroxhyte ( $\delta'$ -FeOOH) by the IMA (Chukhrov et al., 1977).

Ostwald (1984) observed three broad lines at ca. 2.5, 2.2, and 1.4 Å in dark zones of nodules from the Indian Ocean by SAED. The exact positions of these lines vary with the Mn/Fe ratio. In zones with Mn/Fe weight ratios of 0.9 to 1.3, the *d* values of the two outer lines range from 2.61 to 2.64 Å and 1.46 to 1.50 Å, respectively (as in ferrihydrite and ferroxhyte). In zones with Mn/Fe ratios of 1.7 to 2.3, these lines are between 2.41–2.48 Å and 1.41–1.45 Å (as in vernadite). These differences led Ostwald (1984) to conclude that “the dark component of the nodule is apparently a very fine mixture of vernadite and ferrihydrite/ferroxhyte,” but he could not determine which of these two Fe oxides was actually present in this mixture.

<sup>57</sup>Fe Mössbauer spectroscopy is a useful technique for investigating ferromanganese samples because it is specific to Fe, and the other components of a sample act only as diluents. Mössbauer spectroscopy is sensitive to the local atomic environment and is therefore particularly well-suited to characterize poorly crystalline materials. As a result, <sup>57</sup>Fe Mössbauer spectroscopy can play an important role in identifying iron oxide phases in metalliferous sediments.

Some studies of marine ferromanganese nodules making use of Mössbauer spectroscopy have been carried out. In almost all of these studies, spectra were taken only in the paramagnetic state (i.e., at room temperature or 77 K). Although such spectra can be used to determine the oxidation state, Fe coordination, and the Fe<sup>3+</sup> site distortion, they are not mineral-specific (see review by Murad and Johnston, 1987). More useful results can be obtained at 4.2 K. Johnson and Glasby (1969) observed that two manganese nodules from the Indian Ocean order magnetically between 77 and 1.3 K. At 4.2 K, the Mössbauer spectra of these nodules had broad lines and the magnetic hyperfine field was about 50 T. From the superparamagnetic blocking temperatures, the particle diameters were estimated to be about 9 nm and larger; the Fe-bearing component was tentatively identified as either a mixture of goethite and lepidocrocite or another combination of ferric compounds, or a mixed iron-manganese oxide. In a study of Pacific Ocean crusts and nodules, Hryniewicz et al. (1970) observed complete magnetic order with a low hyperfine field of 46 T at 4.2 K and inferred Fe to be bound in a phase resembling “hydrous ferric gels.” Coey and Schindler (1977) arrived at a similar assignment for the ferric component of some freshwater ferromanganese nodules. A more conclusive Mössbauer spectroscopic characterization of this phase has not been given to date.

In this paper we present selective chemical dissolution, X-ray diffraction (XRD), and <sup>57</sup>Fe Mössbauer spectroscop-

ic data for some deep-sea ferromanganese crusts, with the purposes of identifying the iron oxide component and determining whether chemical extraction of manganese oxides and the consequent enrichment of iron oxides allows improved mineralogical characterization of the Fe component of ferromanganese oxides.

### MATERIALS AND METHODS

Three samples of black ferromanganese nodules from the Central Pacific were used for this study. Two of these were collected during the Midpac '81 cruise of the R.V. *Sonne*: sample 217 (=SO33-34DK2) was dredged at 6°17.43'N, 166°57.26'W from a depth of 2020 m, and sample 218 (=SO33-3DK2) at 18°38.09'N, 158°18.56'W from a depth of 2140 m. Sample 219 (=10D7) was collected during a cruise of the S.P. *Lee* at 21°48.00'N, 167°37.17'W from a depth of 2100 m. Before analysis, the 0.5- to 2-mm-thick, hard crusts were gently ground in an agate mortar until they passed through a 60- $\mu$ m sieve.

To determine total Fe and Mn, the samples were digested with a mixture of HF and H<sub>2</sub>SO<sub>4</sub>. Fe and Mn were also dissolved with concentrated HCl at 110 °C and with dithionite-bicarbonate-citrate (Mehra and Jackson, 1960). The dithionite treatment specifically dissolves all Fe and Mn bound in oxides by reduction of Fe<sup>3+</sup> and Mn<sup>4+</sup>. The samples were also extracted with 0.2M ammonium oxalate at pH 3.0 in the dark (Schwertmann, 1964). This method is widely used in soil studies and dissolves all Mn<sup>4+</sup> oxides, but only the poorly crystalline Fe<sup>3+</sup> oxides such as ferroxihite and ferrihydrite. To avoid calcium oxalate formation during oxalate extraction, the samples were pretreated with 0.1M HCl (100-mL solution per 1 g sample) for 2 h at room temperature. This pretreatment removes essentially no Mn and Fe. To concentrate iron oxides, the samples were subjected to eight successive treatments with 0.01M hydroxylamine chloride at pH 4.0 for 2 h at room temperature. This treatment (modified from Chester and Hughes, 1967), reduces Mn<sup>4+</sup> oxides but not the Fe<sup>3+</sup> oxides. All chemical analyses were carried out by atomic-absorption spectroscopy following sample dissolution as described above.

Surface areas were determined by the ethylene glycol methyl ether (EGME) method as described by Carter et al. (1965).

X-ray diffraction was done with a Philips PW1050/70 instrument by counting random powder samples in steps of 0.05° 2 $\theta$  for 100 s per step, using CoK $\alpha$  radiation and a diffracted-beam graphite monochromator. Selected peaks were computer-fitted by using a combination of Gaussian and Cauchy lines (Voigt profile) to obtain more precise *d* values.

Mössbauer spectra were taken on samples comprising 35 mg/cm<sup>2</sup> of untreated or 15 mg/cm<sup>2</sup> of hydroxylamine-treated material at room temperature, 77 K, and 4.2 K using a <sup>57</sup>Co-Rh source moved in a sinusoidal mode. Spectra were collected on 1024 channels of a multichannel analyzer until about 1.5 × 10<sup>6</sup> to 3.2 × 10<sup>6</sup> counts per channel had been accumulated. The data were folded, plotted, and fitted by a computer procedure. Velocity calibration was done using a 6- $\mu$ m-thick metallic Fe foil, and the Mössbauer parameters are given relative to this standard at room temperature. Spectra are plotted as measured.

Preliminary fits of spectra of the paramagnetic material were carried out using one Lorentzian doublet with no constraints on line widths and intensities. For models involving distributions of quadrupole splittings, the spectra were fitted with up to 18 doublets of equal isomer shifts with the splittings increasing in increments of 0.20 mm/s. For these fits, all line widths were fixed at 0.20 mm/s, and corresponding lines were constrained to have equal intensities. Spectra taken in the magnetically ordered state

had broad, asymmetric lines and were fitted with distributions of magnetic hyperfine fields using a model-free, discontinuous hyperfine-field-distribution program similar to that used by Murad and Schwertmann (1980).

## RESULTS

### Chemical data and surface area

Table 1 shows the concentrations of Fe and Mn extracted by the techniques mentioned above. The amounts of Fe and Mn extracted from the untreated samples with HCl are, within the limits of experimental error, identical to the total Fe and Mn concentrations determined after HF-H<sub>2</sub>SO<sub>4</sub> digestion. The untreated samples contain similar amounts of Fe and Mn that range from about 15 to 22 wt%. The dithionite treatment extracts, on an average, 99% of the total Fe and Mn, showing essentially all Fe and Mn to be present in the samples as oxides. The oxalate and dithionite treatments (indicated by subscripts o and d, respectively) remove similar amounts of Fe (giving Fe<sub>o</sub>/Fe<sub>d</sub> ratios close to 1), which is typical for poorly crystalline iron oxides.

The hydroxylamine treatment extracts over 85% of the Mn<sub>d</sub> but less than 1% of the Fe<sub>d</sub>, thereby almost doubling the concentration of Fe in the samples. The Fe<sub>o</sub>/Fe<sub>d</sub> ratios of the hydroxylamine-treated samples are also close to 1.

The surface areas of the untreated samples 217, 218, and 219 are 585, 624, and 692 m<sup>2</sup>/g, respectively. These high values suggest an extremely small particle size.

### X-ray diffraction

All untreated samples show two major lines at 2.45 and 1.42 Å and weaker, broad lines at 2.26 and 1.70 Å (Figs. 1, 2). This set of lines has been observed in numerous studies of Mn crusts and nodules and is usually assigned to a poorly ordered phyllo-manganate called vernadite by Chukhrov et al. (1979) and Chukhrov and Gorshkov (1980) or random-stacked birnessite by Giovanoli (1980). Sample 217 shows two additional, relatively sharp lines at 9.8 and 4.9 Å (Fig. 1), which can be assigned either to busenite (a 10-Å phyllo-manganate) or to the tunnel-structure manganese oxide todorokite. Since the spacing is below 10 Å and persists on air-drying, todorokite seems to be the more likely mineral. The observed manganese oxide mineralogy is in agreement with earlier studies of ferromanganese nodules and encrustations (see, for example, reviews by Glasby, 1972; Burns and Burns, 1979; Cronan, 1980; Usui et al., 1987).

After removal of most of the Mn with hydroxylamine, all samples have broad and strong peaks at 2.5, 2.23, 1.72, and 1.45 Å, plus a weak peak at 4.18 Å indicative of goethite (Figs. 1, 2). Using the Scherrer formula, the half-width of the main peak at 2.5 Å, estimated to be about 10° 2 $\theta$ , would correspond to a particle size of approximately 10 Å. The fact that no peaks are observed at 1.97 Å might be taken to indicate that the hydroxylamine-treated samples contain ferroxihite ( $\delta'$ -FeOOH) rather than ferrihydrite.

Considering that even the two strongest iron oxide peaks at 2.5 and 1.45 Å are barely visible in the original sam-

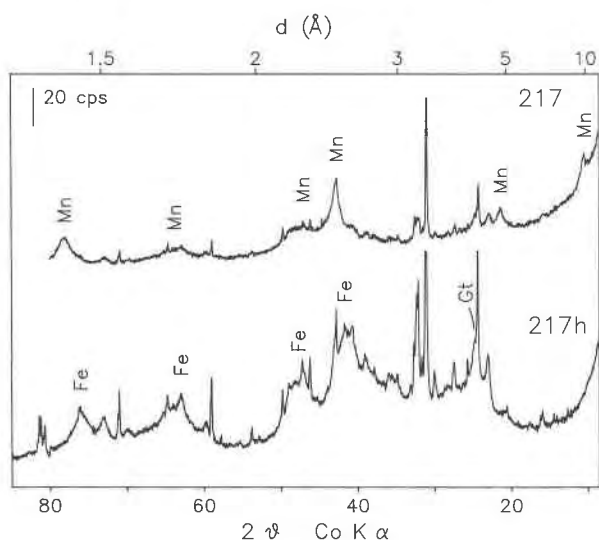


Fig. 1. X-ray diffraction traces of sample 217 (top) before and (bottom) after treatment with hydroxylamine chloride. The peaks designated Mn and Fe are attributed to the manganese and iron oxides; a more detailed characterization of these is given in the text. The main goethite peak at  $4.18 \text{ \AA}$  is marked Gt. The  $x$  axis is calibrated in  $2\theta$  angles and  $d$  values in  $\text{\AA}$ .

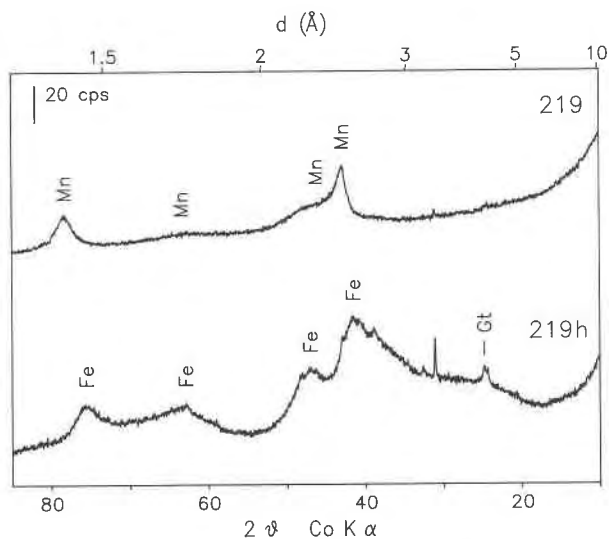


Fig. 2. X-ray diffraction traces of sample 219 (top) before and (bottom) after treatment with hydroxylamine chloride. The peaks designated Mn and Fe are attributed to the manganese and major iron oxides; a more detailed characterization of these is given in the text. The main goethite peak at  $4.18 \text{ \AA}$  is marked Gt. The  $x$  axis is as in Fig. 1.

ples, the relatively high intensities of the iron oxide lines are somewhat surprising, since the hydroxylamine treatment concentrated Fe only by a factor of 2. It is thus conceivable that the removal of Mn with hydroxylamine may also have affected the iron oxide phase.

### Mössbauer spectroscopy

At room temperature, the untreated samples 217 and 219 are completely paramagnetic, giving Mössbauer spectra that consist of relatively broad, unspecific  $\text{Fe}^{3+}$  doublets. The quadrupole splitting for a one-doublet fit averages about  $0.69 \text{ mm/s}$ . Only sample 219 was studied at  $77 \text{ K}$ . Except for a very subordinate, magnetically ordered component with a hyperfine field of  $47.4 \text{ T}$  that can be assigned to goethite (relative area 1.6%), the spectrum of the untreated sample 219 at  $77 \text{ K}$  is essentially the same as that taken at room temperature.

Following hydroxylamine treatment, the quadrupole

splitting of samples 217 and 219 in the paramagnetic state increases slightly (from  $0.69$  to  $0.72 \text{ mm/s}$  for one-doublet fits). The parameters and the relative area of the magnetic component in sample 219 at  $77 \text{ K}$  are the same before and after hydroxylamine treatment.

Fitting the room-temperature spectra of the samples with one Lorentzian doublet, however, is unsatisfactory because of the extremely large line widths and non-Lorentzian line shape. Fitting these spectra with two doublets gives an improved delineation of the data, but such a model implies two *discrete* Fe sites. We obtain the best fits using distributions of Lorentzian doublets, which are more realistic and allow a rational parametrization of the data (Murad and Johnston, 1987; Murad and Schwertmann, 1988).

Values for one-doublet fits and quadrupole-distribution fits (Table 2) show increases in the maxima of the distributions following Mn removal with hydroxylamine chloride (Figs. 3, 4), paralleling the differences in average

TABLE 1. Fe and Mn concentrations of the three manganese crusts studied (both untreated and after hydroxylamine treatment)

Sample*	$\text{Fe}_t^{**}$	$\text{Fe}_d^{**}$	$\text{Fe}_o^{**}$	$\text{Fe}_h^{**}$	$\text{Mn}_t^{**}$	$\text{Mn}_d^{**}$	$\text{Mn}_o^{**}$	$\text{Mn}_h^{**}$
217	15.3	14.9	13.3	0.12	18.1	17.7	17.4	15.6
217h		28.4	24.0			2.8	2.8	
218	18.0	17.8	17.1	0.14	15.1	15.1	14.8	13.5
218h		30.5	29.6			1.7	1.9	
219	15.3	15.1	14.5	0.04	22.2	22.3	20.9	19.9
219h		37.6	35.6			2.4	2.9	

Note: Values give wt% of total Fe and Mn and of Fe and Mn extracted by the different chemical treatments.

\* Samples with numbers ending with "h" were subjected to hydroxylamine chloride extraction before analysis.

\*\* Subscripts refer to total concentrations for HF dissolution (t) and amounts extracted by sodium dithionite (d), ammonium oxalate (o), and hydroxylamine chloride (h).

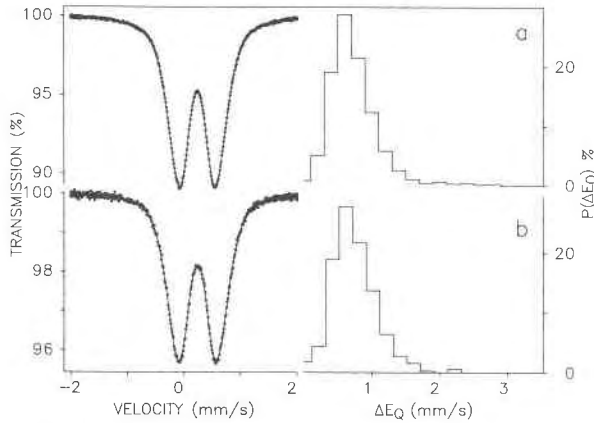


Fig. 3. Room-temperature Mössbauer spectra of sample 217 (a) before and (b) after treatment with hydroxylamine chloride and quadrupole-splitting distributions derived from these spectra.

quadrupole splittings from one-doublet fits. The half-widths of the distributions also increase following the hydroxylamine treatment, indicating a higher variability of environments of the Fe atoms.

Mössbauer spectra taken at 4.2 K indicate almost complete magnetic order in sample 217 (Fig. 5) and complete magnetic order in sample 219 (Fig. 6). The spectra have broad, asymmetric lines. One-sextet fits give average outer line widths of about 1.4 mm/s and magnetic hyperfine fields of 46.1 and 45.4 T, respectively (Table 3). The spectral lines are broader and the fields lower than those observed for even the most poorly crystallized, chemically pure ferrihydrites (Murad and Schwertmann, 1980; Murad, 1982) and resemble those of siliceous ferrihydrite + allophane assemblages in young volcanic soils (Murad and Schwertmann, 1988).

To be adequately characterized, these spectra must be fitted with distributions of magnetic hyperfine fields rath-

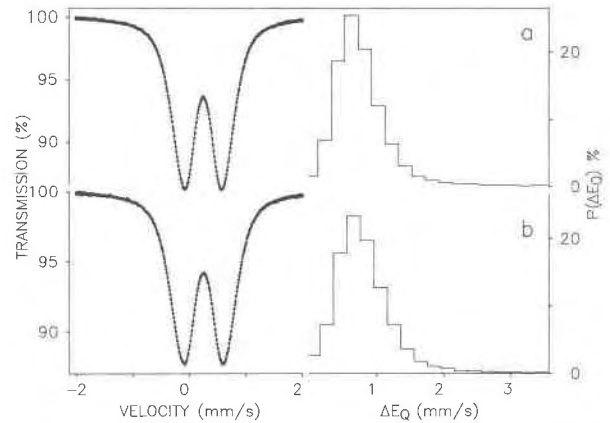


Fig. 4. Room-temperature Mössbauer spectra of sample 219 (a) before and (b) after treatment with hydroxylamine chloride and quadrupole-splitting distributions derived from these spectra.

er than discrete fields. Fitting the 4.2-K spectrum of sample 217 with a distribution of hyperfine fields indicates the maximum of the field distribution to be at 46.2 T and the distribution to have a half-width of 8.3 T. The relative area of the paramagnetic component is 3%. Following hydroxylamine treatment, the maximum of the hyperfine-field distribution shifts significantly to 48.3 T, and the distribution narrows to a half-width of 6.2 T (Table 3). The paramagnetic component is not affected by the hydroxylamine treatment, indicating that this component is due to silicate-bound  $\text{Fe}^{3+}$  (Fig. 5). Similarly, the maximum of the hyperfine-field distribution of sample 219 shifts from 45.6 to 48.1 T, and the distribution narrows from 8.1- to 6.7-T half-width following the hydroxylamine treatment (Table 3; Fig. 6).

## DISCUSSION

Mössbauer spectra of the untreated ferromanganese crusts in the paramagnetic state at room temperature and 77 K can be fitted with distributions of quadrupole-split doublets with average maxima of the quadrupole-splitting distributions at 0.63 mm/s. This quadrupole splitting is higher than those of well-crystallized iron oxides in the paramagnetic state (about 0.5 mm/s) and indicates a moderately high average distortion of Fe sites. Although it is not *diagnostic* for a specific mineral, it could result from ferroxhite or relatively well crystallized, unsubstituted ferrihydrite.

At 4.2 K, the untreated samples have wide distributions of magnetic hyperfine fields with extremely low fields of maximum probability (averaging 45.9 T). These hyperfine fields are considerably lower than those observed by Koch et al. (1987) at 5 K for microcrystalline ferroxhites (49.6 T for about 20-Å-thick particles). The low hyperfine fields and the high widths of the hyperfine-field distributions thus indicate that the iron oxide phase of the described ferromanganese crusts consists of ferrihydrite of extremely poor crystallinity. The sign of the

TABLE 2. Parameters of different fits to room-temperature Mössbauer spectra

Sample	Fit*	$\Delta E_Q$	$\delta/\text{Fe}$	$W$	$A$	$\chi^2$
217	1D	0.672(1)	0.357(1)	0.414(1)	1.00	13.87
	QD	0.61(2)	0.357(1)	0.62	0.29(1)	1.12
217h	1D	0.705(1)	0.361(1)	0.423(3)	1.00	3.38
	QD	0.63(2)	0.360(1)	0.66	0.28(1)	0.83
219	1D	0.701(1)	0.358(1)	0.447(1)	1.00	35.54
	QD	0.64(2)	0.357(1)	0.69	0.25(1)	1.88
219h	1D	0.744(1)	0.361(1)	0.477(1)	1.00	22.79
	QD	0.67(2)	0.360(1)	0.76	0.23(1)	1.56

Note: Values are quadrupole splittings ( $\Delta E_Q$ ), isomer shifts ( $\delta/\text{Fe}$ ), line widths ( $W$ ) in mm/s, and relative areas ( $A$ ) given by different fits to the room-temperature Mössbauer spectra of samples 217 and 219 before and after (217h, 219h) hydroxylamine treatment. Errors on the last digit given in parentheses.

\* 1D = one-doublet fits, QD = quadrupole-distribution fits. For the latter,  $\Delta E_Q$  represents the quadrupole splitting class with maximum probability,  $W$  the half-width of the distribution, and  $A$  the relative area of the class representing the maximum of the distribution.  $\chi^2$  is a measure for the quality of the fit.

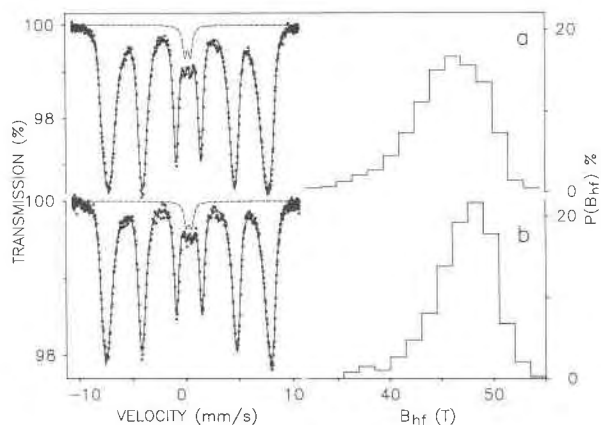


Fig. 5. Mössbauer spectra of sample 217 taken at 4.2 K (a) before and (b) after treatment with hydroxylamine chloride and hyperfine-field distributions derived from these spectra. The paramagnetic doublet subspectra remaining at 4.2 K are indicated with broken lines.

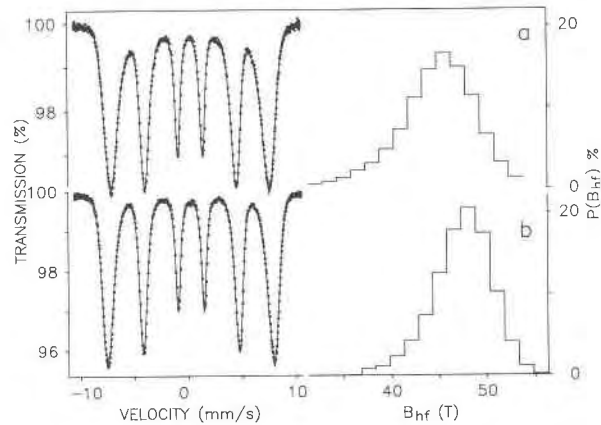


Fig. 6. Mössbauer spectra of sample 219 taken at 4.2 K (a) before and (b) after treatment with hydroxylamine chloride and hyperfine-field distributions derived from these spectra.

quadrupole interaction at 4.2 K ( $-0.05$  mm/s) is also in favor of ferrihydrite rather than feroxyhite (about  $+0.05$  mm/s).

The apparent conflict between the Mössbauer data for the paramagnetic and the magnetically ordered material can be resolved if the main Fe-bearing phase is considered not to consist of isolated ferrihydrite particles, but rather to have a hybrid structure in which ferrihydrite and Mn oxides are irregularly intergrown (as postulated by Ostwald, 1984). Such a structure would make this material geometrically more regular than an unsupported ferrihydrite of very poor crystallinity, so that the Fe sites would be less distorted and the quadrupole splitting in the paramagnetic state consequently lower. The low hyperfine field could result either from an extremely small size of the magnetically coherent ferrihydrite particles or Mn-for-Fe substitution. On the basis of EXAFS evidence, Manceau and Combes (1988), however, recently showed that the Fe and Mn phases in an Fe-containing vernadite are not isostructural, thus ruling out the existence of Mn-for-Fe substitutions on an atomic scale.

An intergrowth of iron and manganese oxides could still cause some reduction of magnetic superexchange interactions in the magnetically ordered state (because  $\text{Fe}^{3+}$  has five  $3d$  electrons, whereas  $\text{Mn}^{2+}$  has only three  $3d$  electrons and thus a smaller magnetic moment), and thereby reduce hyperfine fields. Work on Mn-substituted hematites and goethites by Vandenberghe et al. (1986), however, has shown that Mn substitution does not reduce magnetic hyperfine fields as drastically as, for example, Al substitution. It is therefore likely that small particle size is the predominant mechanism causing the low magnetic hyperfine field in samples 217 and 219 at 4.2 K.

Following selective removal of manganese oxides with hydroxylamine, the intensities of the four broad xrd peaks attributed to iron oxides (Figs. 1, 2) increased disproportionately. This change cannot be due simply to the two-fold increase in the relative concentration of iron oxides indicated by the chemical analyses (Table 1). In the original samples, the iron oxide particles appear to lack coherence, probably owing to their intimate association with manganese oxides. A higher degree of coherence, leading to the development of broad but significantly stronger xrd lines, is attained after removal of the manganese

TABLE 3. Parameters of different fits to the Mössbauer spectra at 4.2 K

Sample	Fit*	$B_{hf}$	$\Delta$	$\delta/\text{Fe}$	$W$	$A$	$\chi^2$
217	1S	46.1(1)	-0.059(2)	0.487(1)	1.36(1)	1.00	9.90
	SD	46.2	-0.070(2)	0.484(1)	8.3	0.17(1)	2.70
217h	1S	47.6(1)	-0.070(3)	0.492(2)	1.09(1)	1.00	3.59
	SD	48.3	-0.080(3)	0.489(2)	6.2	0.22(1)	1.45
219	1S	45.4(1)	-0.040(2)	0.485(1)	1.41(1)	1.00	8.41
	SD	45.6	-0.040(2)	0.485(1)	8.1	0.17(1)	2.27
219h	1S	47.7(1)	-0.050(1)	0.486(1)	1.18(1)	1.00	14.56
	SD	48.1	-0.051(1)	0.485(1)	6.7	0.21(1)	3.18

Note: Hyperfine fields ( $B_{hf}$ ) in teslas, quadrupole interactions ( $\Delta$ ), isomer shifts ( $\delta/\text{Fe}$ ), line widths ( $W$ ) in mm/s, and areas ( $A$ ) in proportion of the total area of different fits to the Mössbauer spectra of samples 217 and 219 before and after (217h, 219h) hydroxylamine treatment taken at 4.2 K. Errors on the last digit given in parentheses.

\* 1S = one-sextet fits, SD = sextet-distribution fits. For the latter,  $B_{hf}$  represents the hyperfine-field class with maximum probability,  $W$  the half-width of the distribution (both in teslas), and  $A$  the relative area of the class representing the maximum of the distribution. The error in the hyperfine field of maximum probability is about 1 T.

oxides. This result indicates that at least some reorganization of the iron oxide particles has taken place during the hydroxylamine treatment.

Following hydroxylamine treatment, the Mössbauer spectra show a slight shift in the maxima of the quadrupole distributions in the paramagnetic state (to 0.65 mm/s) and a significant increase in the maxima of the magnetic hyperfine-field distributions (to 48.2 T). The Mössbauer characteristics of the original samples are thus reversed upon Mn removal: the site distortion increases, whereas the magnetic coupling is enhanced. The Mössbauer parameters of the hydroxylamine-treated material both in the paramagnetic and in the magnetically ordered states resemble those of unsubstituted ferrihydrites of intermediate crystallinities (Murad et al., 1988) rather than ferroxhyte (as indicated by XRD).

The extraction of manganese oxides from the studied ferromanganese crusts using hydroxylamine chloride thus obviously causes the iron oxide mineralogy to change. Therefore, use of this reagent cannot be recommended for the selective enrichment of iron oxides in these materials.

#### ACKNOWLEDGMENTS

We are indebted to Prof. P. Halbach, Technische Hochschule Clausthal (Germany) for supplying the samples, Prof. F. E. Wagner, Technische Universität München, for providing access to the low-temperature Mössbauer facilities, Dr. F. T. Manheim (Woods Hole, Massachusetts) for helpful comments, and Mrs. U. Maul for laboratory work. This study has been supported by the Deutsche Forschungsgemeinschaft.

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MANUSCRIPT RECEIVED JANUARY 13, 1988

MANUSCRIPT ACCEPTED JUNE 23, 1988