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Mössbauer spectra of goethite: evidence for structural imperfections

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SUMMARY. Goethites of well-crystallized appearance from a sedimentary ore deposit have been studied by Mössbauer spectroscopy and other methods following HCl corrosion, particle size fractionation, and annealing treatments.

The goethites contained an appreciable amount of Si, but were not significantly Al-substituted. The observed broad and asymmetric resonant lines of the Mössbauer spectra are considered to result from this Si which, interspersed in the goethite structure, would interrupt magnetic coupling and give rise to a reduced and inhomogeneous magnetic hyperfine field.

BELOW its Néel temperature of 393 °K goethite is, in sufficiently large particles ($\gg 100$ Å), antiferromagnetic. At room temperature the Mössbauer spectrum of bulk goethite should therefore consist of six resonant peaks of Lorentzian shape. Most goethites, however, give Mössbauer spectra of rather poor quality. Even macroscopically well-crystallized specimens often have wide lines with shapes that deviate considerably from the Lorentzian.

Numerous explanations have been forwarded to account for this phenomenon. Hrynkiewicz and Kulgawczuk (1963) fitted two superimposed six-line patterns to Mössbauer spectra of goethite and postulated the existence of two interpenetrating sublattice sets of different hyperfine magnetic field. In view of the low resolution of the Mössbauer apparatus used (*c.* 100 channels) and the obviously only moderate counting statistics, this appears to be an over-interpretation of the presented data which, in fact, indicate only the existence of *wide* (but not split) absorption maxima. This concept that goethite possesses two hyperfine magnetic fields has been somewhat uncritically accepted and disseminated further in numerous other papers. Dézsi and Fodor (1966) also fitted two hyperfine fields to Mössbauer spectra of some goethites. Although here, again, the splitting does not appear to be statistically significant, goethites with wide lines ('split spectra') were found to contain water in excess of the theoretical value, whereas stoichiometrically composed samples showed narrower absorption maxima. Thermal analysis and magnetic susceptibility data confirm the existence of different hydration states of goethite (Oosterhout, 1964). Forsyth *et al.* (1968) observed that heating to 160 °C significantly narrowed the Mössbauer lines of a synthetic hydrothermal goethite and interpreted this as a sign of strain annealing. Govaert *et al.* (1976) took Mössbauer spectra of goethites from a variety of natural environments. They suggested that poor Mössbauer spectra of this mineral result from outer regions of gradually decreasing hyperfine field in the individual particles surrounding relatively well-crystallized cores. Mørup *et al.* (1976) showed that asymmetric Mössbauer line shapes can be explained by the distribution of particle sizes alone, though surface effects (e.g. adsorption of organic molecules) may also affect the spectra.

Experimental

The material studied was collected from the Cerro del Hierro open pit mine in south-western Spain (Province of Sevilla). Economic minerals of this sedimentary deposit, formed in Cambrian limestone karst, are colloform goethite and specularitic hematite, with magnetite and recrystallized calcite as minor components. Scattered baryte, Cu-Fe sulphides, and malachite occurring at lower levels of some ore pockets are probably altered detritus of neighbouring mineral veins. Weathering of such veins may also have provided the iron precipitates constituting the deposit proper.

Goethite needles and botryoids of different morphology, hematite, massive ore and interstitial fines were hand-picked for analysis and ground in an agate ball mill. 1 g portions of one botryoidal goethite specimen (802NGT2) were immersed in 0.1 to 0.5N HCl at temperatures between 20 and 50 °C for periods between 19 and 165 hours. This treatment resulted in dissolution of 2 to 32% of the original material. Other treatments include heating to 150 °C followed by cooling at different rates, particle size fractionation by centrifuging, and calcination at 1000 °C.

For the Mössbauer experiments a $^{57}Co/Rh$ source of *c.* 10 mCi was mounted on a loudspeaker-type drive system providing a sinusoidal motion. Sample quantities giving constant Fe concentrations of 12 mg/cm^2, spread uniformly over an area of 2 cm^2 in a plexiglas die, served as absorbers. The transmitted radiation was recorded by a proportional counter and fed into a commercial 1024 channel analyser. The recorded spectra were processed by a computer procedure. Pure metallic iron was used as a standard for velocity calibration.

X-ray diffraction was carried out on texture-free samples mounted in plexiglas holders. The Philips instrument was operated with a Co tube. A graphite monochromator served to remove radiation other than Co-$K\alpha$. Diffractograms were taken in the 2θ range from 18 to 50° (corresponding to d-values from 5.7 to 2.1 Å) at a scanning speed of $\frac{1}{8}°2\theta$/min. To estimate the Al content of the goethites a precise determination of the 111 spacing was effected. $Pb(NO_3)_2$ was added to the samples as an internal standard, the 311 peak of this compound being used for 2θ calibration. Peak positions were located by point counting every 0.005° and the radiation v. 2θ data computer fitted with polynomial functions.

DTA curves were run on a Linseis L62 instrument heating 60 mg samples at a constant rate of 5 °C/min in a nitrogen atmosphere. Calcined hematite was used as inert substance.

Infra-red absorption spectra were recorded from 1:300 KBr disks with a Beckman IR-20A spectrometer.

Fe, Al, Cu, Zn, and Si contents of the goethites were determined by atomic absorption after sample dissolution in concentrated HCl.

Electron micrographs were taken with a Zeiss EM10 microscope operated at 80 kV.

Results

Mössbauer spectroscopy. Room temperature Mössbauer spectra of the ground goethites show the asymmetric peak profiles typical of this mineral (fig. 1). Hematite spectra are superimposed upon those of goethite (corresponding, for example, to 4.3% hematite in the untreated bulk sample 802NGT2, fig. 1*a*). HCl attack results in preferred dissolution of hematite and consequently in diminution of the peaks from this mineral. The hematite spectra can be removed by a computational stripping procedure, improving resolution of the remanent goethite spectra (fig. 1*b*).

Mössbauer parameters of the sample 802NGT2, following the different chemical and physical treatments, are listed in Table I. Because of the line asymmetry the parameters were obtained by a graphic procedure. The values for isomer shift, quadrupole splitting, and hyperfine magnetic field lie in the range normally expected for moderately well-crystallized goethites and reveal no distinct trends. There is no overt evidence for the existence of two discrete hyperfine fields. It rather appears that a distribution of hyperfine fields exists, which has its maximum close to the highest H_i value. On the basis of a calibration curve set up for synthetic aluminous goethites (to be published elsewhere), this H_i value corresponds to an Al substitution of roughly 1%.

Line widths were found to vary systematically following sample treatment. In Table I values are given for the widths of the outer peaks only, as the variations of the inner peaks conform to those of the outer ones in all cases. Because of the line asymmetry the outer peaks were divided by vertical lines through the maxima, giving external ($W_e/2$) and internal ($W_i/2$) half widths.

HCl attack can be seen to result in a narrowing of the lines (i.e. in an improved resolution, fig. 1*c*). Thorough regrinding of sample NGT2C (18% dissolution loss) again increased line widths (NGT2CN, Table I). The widening is particularly prominent in the external half-widths because the wider internal halves can more readily absorb the relatively modest variations concerned. The annealing procedures (Table I, sample NGT2S/T) had no narrowing effect upon the lines.

Particle size classes < 0.075 and > 0.2 μm were separated from a ground sample by centrifuging. Mössbauer spectra show the finer sample to have a significant paramagnetic component, visible in a pronounced deviation from the base line and a zone of increased absorption between the inner peaks (fig. 1*d* and *e*). Neither the line widths nor the hyperfine fields of these fractions, however, differ substantially. The coarse fraction has a hematite content comparable to that of the bulk sample, whereas this mineral seems to be absent from the fraction < 0.075 μm.

Portions of the untreated goethite and that which had suffered 32% dissolution loss were calcined at 1000 °C. Mössbauer spectra of the hematites thus produced gave hardly different hyperfine fields averaging 516.1 kOe. A natural hematite from the same mine had a hyperfine field of 517.5 kOe. Compared with synthetic standards these correspond to Al substitutions of about 4 and 2%, respectively.

The ore material may locally contain significant proportions of magnetite (fig. 1*f*).

X-ray diffraction. The d_{111} value of goethite in both the HCl-treated and untreated samples aver-

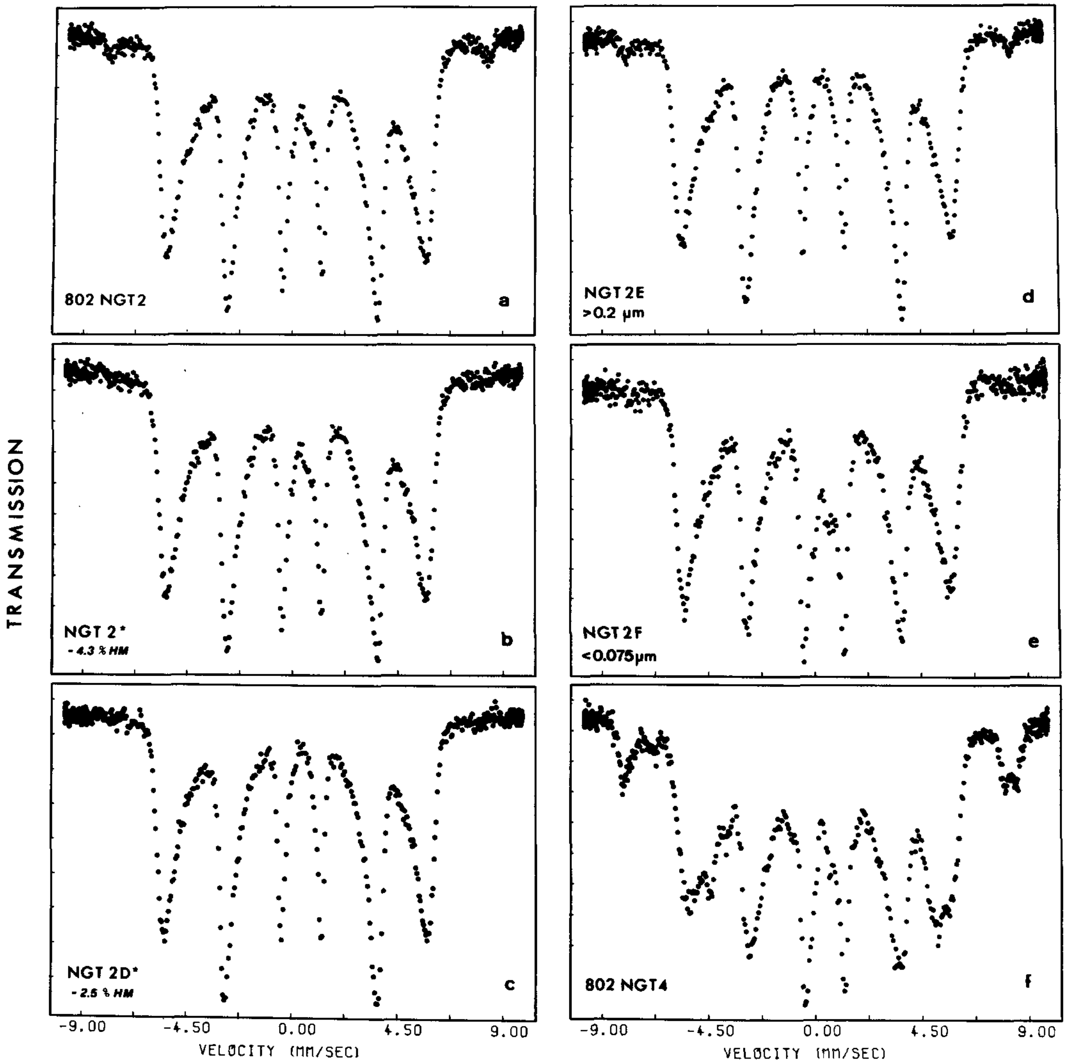

FIG. 1. *a–e*. Room temperature Mössbauer spectra of botryoidal goethite 802NGT2. *a*. Ground but otherwise untreated sample. Superimposed upon the goethite spectrum is that of hematite, the outer lines of which are clearly discernible. *b*. Same spectrum, computationally stripped of the hematite component (4.3%). *c*. HCl-corroded sample NGT2D (dissolution loss 32%), stripped of hematite (2.5%). *d*, *e*. Coarse and fine centrifuge-separated fractions. A superparamagnetic component shows in the centre of the fine fraction. *f*. Fine ore material NGT4, comprising goethite with subordinate hematite and magnetite.

aged 2.4521 ± 0.0003 Å, no systematic variation ensuing from HCl dissolution. If this spacing is interpreted in terms of an isomorphous replacement of Fe by Al, such a substitution would amount to about 1.4% (Thiel, 1963; Jónás and Solymár, 1970; D. G. Schulze, unpubl. results) uniformly throughout the individual particles.

Line widths, averaged over the seven strongest goethite lines in the scanned range, decrease following HCl attack. These fall from 0.41°2θ for a ground but otherwise untreated sample to 0.38° for that which had suffered 32% loss by dissolution (fig. 2).

Of the particle size fractions separated by centrifuging, the coarser (> 0.2 µm) had half widths of 0.40° and the finer (< 0.075 µm) 0.50°2θ. These values overlap only partly with the range covered by HCl dissolution, the line narrowing associated with corrosion proceeding further.

Line widths of calcite and magnetite, where

TABLE I. *Mössbauer parameters of pulverized goethite 802NGT2 following different treatments*

Sample	Dissolution loss %	Particle size fraction μm	Annealing temp. °C	H_i	δ	ΔE_Q	$W_e/2$	$W_i/2$
NGT2	—	total	—	357	0.38	0.29	0.31	0.79
NGT2A	2	total	—	356	0.34	0.27	0.30	0.78
NGT2B	6	total	—	359	0.37	0.25	0.30	0.80
NGT2C	18	total	—	358	0.36	0.27	0.29	0.75
NGT2D	32	total	—	361	0.36	0.26	0.28	0.73
NGT2E	—	> 0.2	—	361	0.34	0.28	0.32	0.75
NGT2F	—	< 0.075	—	359	0.37	0.27	0.34	0.77
NGT2S/T	—	total	150	359	0.36	0.25	0.33	0.76
NGT2DS	32	total	150	362	0.36	0.26	0.30	0.80
NGT2CN	18	reground	—	362	0.38	0.28	0.35	0.76

δ	Isomer shift (mm s^{-1}) referred to metallic iron.
ΔE_Q	Quadrupole splitting (mm s^{-1}) = (splitting$_{12}$ − splitting$_{56}$)/2.
H_i	Hyperfine magnetic field (kOe) recalculated to 295 °K.
$W_e/2$	Width of external portion of peaks 1 and 6 at half maximum.
$W_i/2$	Width of internal portion of peaks 1 and 6 at half maximum.

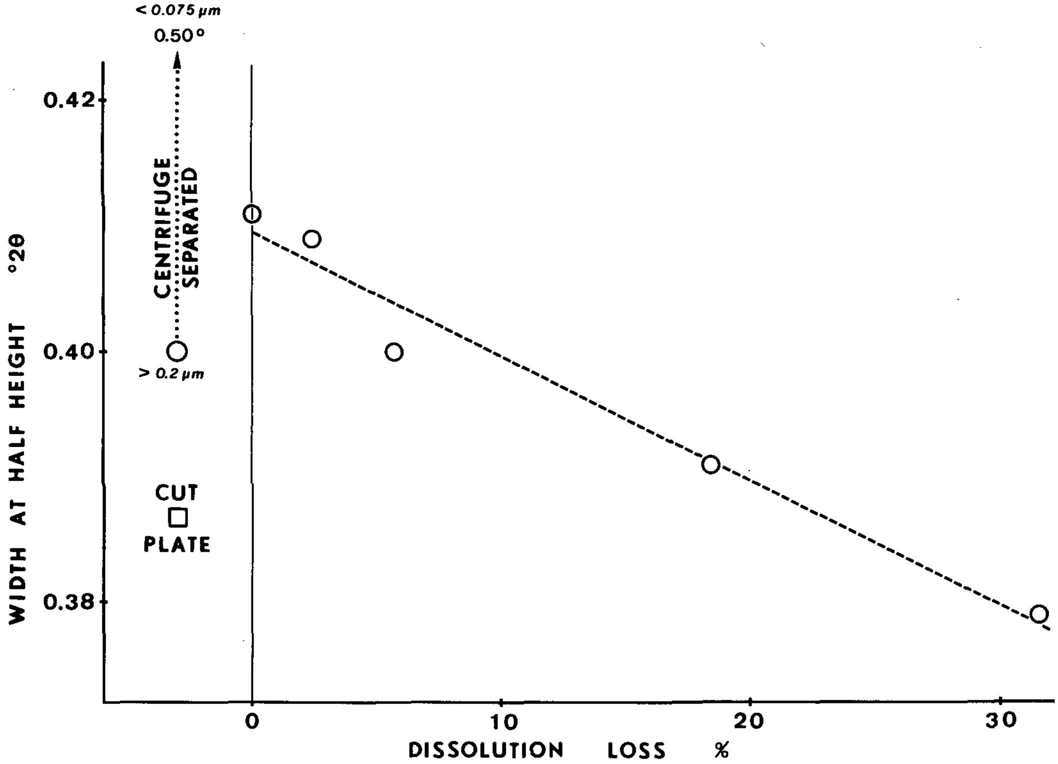

FIG. 2. X-ray diffraction line widths of sample NGT2 in the 2θ range from 20–50° following mechanical (*left*: cut-and-ground + centrifuge-separated samples) and chemical (HCl corrosion) treatment.

present in composite samples, do not—in contrast to goethite—deviate substantially from the instrumental line width (*c.* 0.22°2θ).

Hematite, shown by Mössbauer spectroscopy to be present in all samples from this deposit, could not be properly determined by XRD due to interference from goethite. The hematite line at 3.67 Å, not subject to interference, was too weak to be discerned at the low concentrations concerned.

Differential thermal analysis. DTA curves of the sample 802NGT2 were obtained at different degrees of pulverization and following the abovementioned treatments. An unground specimen showed only one, though asymmetric, endothermic peak at 315 °C. The temperature of this 'upper' peak remains the same throughout the whole treatment sequence. When the specimen consists of fibres less than 1 mm in diameter, broken off with a spatula, a second peak can be discerned at about 290 °C. The temperature of this peak is reduced, i.e. the separation of the two peaks increases, when the sample is ground, and it is reduced further if grinding is followed by HCl attack, down to a minimum of about 280 °C. At the same time the height of the low temperature peak increases and that of the upper one decreases (fig. 3).

The positions of these peaks for the coarse fraction (> 0.2 μm) separated by centrifuging resemble those of the unground fibrous (< 1 mm) specimen. The annealing procedure also tends to reduce the peak separation effected by grinding the sample.

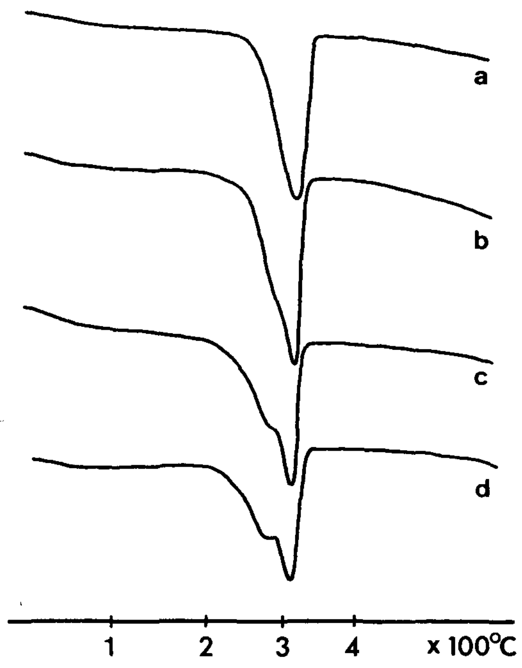

FIG. 3. DTA curves of goethite NGT2. *a.* Unbroken sample (one chunk only). *b.* Broken but not ground sample. *c.* Ground sample. *d.* Ground and HCl-corroded sample NGT2B (dissolution loss 6 %).

Infra-red spectroscopy. The samples 802NGT2 and NGT2D (HCl dissolution loss 0 and 32 %, respectively) gave practically identical IR spectra with absorption maxima at 3180, 890, 790, 655, 610, 450, 410, and 370 cm^{-1}.

IR spectra of a synthetic Si-containing goethite with an Si/Fe ratio of 0.4 %, prepared by converting lepidocrocite to goethite in the presence of Si (Schwertmann and Taylor, 1972), showed good agreement with the natural samples studied.

The positions of the high-temperature DTA peak and the IR absorption maximum near 900 cm^{-1} agree with data by Jónás and Solymár (1970) for synthetic Al-poor ($\leqslant 4\%$ substituted) aluminous goethites. Values given in that paper average 310 °C and 895 cm^{-1}, respectively, both parameters increasing substantially with rising Al substitution.

Chemical analysis. HCl-corroded and untreated specimens of the sample 802NGT2 were dissolved in concentrated HCl. The Fe content of the untreated sample was 62.8 %. All samples had rather low Al contents, averaging 0.03 %. This corresponds to a molar Al/Fe substitution of roughly 0.1 %. Concentrations of Zn and Cu, which locally form individual minerals in the deposit, were 90 and < 4 ppm, respectively.

To ensure that no abraded material from the agate mill used for sample grinding falsifies the determination of Si, specimens analysed for this element were only broken with a hammer on a steel plate. Silicon set free following HCl dissolution forms a gelatinous precipitate. This was separated from the solution by centrifuging and dissolved in 4N NaOH (in which it was readily soluble). After neutralization with 1N H_2SO_4, Si was determined by AAS. The concentration of Si in the sample 802NGT2 was 0.44 %, giving a molar Si/Fe ratio of 0.014.

Heating the samples to 150 °C (during annealing) resulted in a weight loss of 1.3 %. Such an annealed sample lost further 11.6 % on ignition at 1000 °C; distinctly more than the theoretical loss of 10.1 %.

Discussion

The needle iron ore and botryoidal goethite investigated consist of radial, apparently well-developed crystals. Much of the data presented above, however, indicates the goethites to be of a rather modest crystallinity. Both the Mössbauer and X-ray diffraction lines are disproportionately wide. This may—at least in part—be a particle size phenomenon, arising from the presence of some ultra-fine material. The properties of such material are exemplified by the data for the centrifuged fraction < 0.075 μm (see figs. 1*f* and 2). Sample NGT2CN, produced by regrinding the corroded sample NGT2C, shows that such wide lines may also be the outcome of excessive sample comminution (Table I).

In this connection it is necessary to make a fundamental distinction between domain sizes inherent as a result of crystal dimensions in the bulk sample (or the sizes of physically and chemically homogeneous zones, if these are smaller) and particle sizes created by grinding the sample. If sample grinding proceeds beyond the natural crystal size, a distribution of particle sizes caused by the grinding will be superimposed upon the former. Pulverization of samples for study by physical methods should therefore be as mild as possible.

The XRD line widths of the fraction > 0.2 μm exceed the instrumental width. Though small particles produce broad lines, such an effect can also result from a distribution of positions for each diffraction line. Distinction between these two cases is possible only when such a distribution leads to asymmetric line broadening. This was not the case here. The strongly HCl-corroded samples had narrower XRD lines than the coarse fraction. Electron micrographs show this to result from the preferred dissolution of fine particles during corrosion (fig. 4*a*, *b*), whereas remnants of such fine material still adhere to the coarse particles following centrifuging (fig. 4*c*).

The DTA curve given by a single fragment of the botryoidal goethite 802NGT2 shows only one endothermic peak at 315 °C, which is asymmetrically broadened towards lower temperatures. A separate lower-temperature peak first appears following a very mild form of sample comminution. This indicates inhibition of the dehydration in the unground sample, possibly due to lack of escape conduits in that state. An internal water pressure may build up until dehydration takes place, more or less suddenly, when the sample can no longer withstand this pressure. If the sample is ground, release of loosely bound water can take place more readily at the correct temperature. In pulverized samples escape channels for water may be superficially clogged up by ultra-fine material. This will result in a retarded dehydration, causing the low-temperature peak to be partly suppressed and displaced to higher temperatures. If such ultra-fine material is removed by etching, resolution will improve, and the—obviously inherent—doublet show up.

The X-ray line positions and hyperfine magnetic field of the goethites studied are shifted from the values for the pure mineral. A possible explanation for this phenomenon is given by the chemical analysis, which, for example, shows the sample 802NGT2 to have Al/Fe and Si/Fe mole ratios of 0.001 and 0.014, respectively.

The decrease in lattice dimensions associated with Al substitution in goethite results from the smaller radius of the Al^{3+} ion (0.51 Å) compared to that of Fe^{3+} (0.64 Å). Si^{4+} (0.42 Å), often replaced by Al^{3+} in silicate minerals, has been shown to occur amply in goethites (Norrish, 1975). Replacement of Fe by Si should change lattice dimensions in the same sense as the better-known substitution of Al for Fe, though the larger difference in ionic radii may set narrower limits to a substitution of Si for Fe than when Al replaces Fe (Schwertmann and Taylor, 1977).

Whether Fe^{3+} is replaced by Al^{3+} or Si^{4+}, the

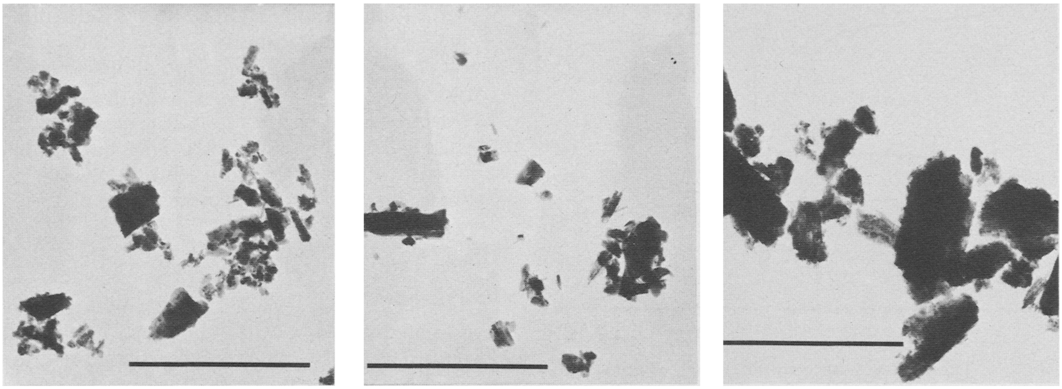

FIG. 4. Electron micrographs of ground goethite NGT2. Scale bar represents 1 μm. *a*. Total sample. *b*. HCl-corroded sample NGT2D (dissolution loss 32 %). *c*. Centrifuge-separated fraction > 2 μm.

effect on the magnetic hyperfine field is the same, since neither of the latter ions has a magnetic moment. The net change will be an interruption of the regular magnetic arrangement and consequently a reduction of the hyperfine field. If such foreign ions are irregularly interspersed in the structure they will result in a distribution of magnetic hyperfine fields downwards from a maximum corresponding to the pure α-FeOOH phase. A magnetically split Mössbauer spectrum will disclose relations of this kind by an assymmetric broadening of the resonant lines.

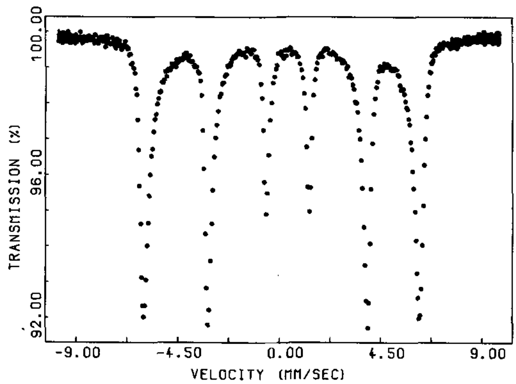

FIG. 5. Room temperature Mössbauer spectrum of fibrous goethite from Western Australia.

A Mössbauer spectrum of relatively good quality was obtained for a fibrous goethite from Western Australia (fig. 5). Microprobe analysis of this material led to the detection of only Fe (W. J. McHardy, Aberdeen, pers. comm.). A determination of Si by AAS gave a value of 0.08%, considerably less than that of the goethites studied here. These possess the broad and asymmetric lines predicted above for substituted goethites. Comparison of the centrifuge-separated fractions shows this to be no particle size effect. The HCl dissolution causes a minor narrowing of the Mössbauer peaks, probably due to preferential dissolution of zones of poor crystallinity (as indicated by the XRD and DTA measurements). The remaining line broadening (fig. 1*c*) is considered to be due to non-stoichiometry.

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