NOTES

TETRAHEDRAL Fe^{3+} IN FERRIHYDRITE: ^{57}Fe MÖSSBAUER SPECTROSCOPIC EVIDENCE

Recently Eggleton and Fitzpatrick (1988) presented a revised structural model for the hydrous iron oxide ferrihydrite. They used a number of analytical techniques to provide evidence that 6-line (by X-ray powder diffraction) ferrihydrite contained ~36% Fe in tetrahedral sites. They also suggested that the Mössbauer spectroscopic work of Murad and Schwertmann (1980) shows that the paramagnetic resonance of ferrihydrite can be well fitted by two doublets with Lorentzian lineshapes. Murad and Schwertmann (1980) also showed that the magnetically ordered spectra of ferrihydrites recorded at 4 K can be fitted by a number of sextets having similar isomer shifts (δ) and a range of slightly differing magnetic hyperfine fields. They concluded that their results indicated F^{3+} was not necessarily present in a number of discrete sites, but that the Mössbauer spectra more likely resulted from a continuum of Fe^{3+} sites having slightly different types and arrangements of neighboring ions, i.e., O, OH, and/or OH$_2$.

As noted by Murad and Schwertmann (1980) and other workers (e.g., Childs and Johnston, 1980; Lewis and Cardile, 1988) fitting two doublets to the paramagnetic room temperature spectrum of ferrihydrite does give an acceptable fit; upon fitting a third doublet and successive doublets, however, the χ^2 value used to measure the statistical acceptability of the fit is not usually significantly further improved. Murad and Johnston (1987) demonstrated that a distribution of doublets with a range of quadrupole splitting (Δ) values may be fitted to the paramagnetic spectrum for a 2-line ferrihydrite. Murad (1987) also showed that such a distribution with a large number of doublets (18) may be fitted to the paramagnetic spectra of other octahedral Fe^{3+} substituted minerals such as nontronite.

Mössbauer spectroscopy is highly sensitive to the state of coordination of the ^{57}Fe nucleus and should thus be capable of discerning whether Fe is tetrahedrally or octahedrally coordinated, as has been demonstrated, for example, for montmorillonites and nontronites (Cardile and Johnston, 1985, 1986). To date, published Mössbauer spectra for ferrihydrite have only been fitted with doublets corresponding to Fe^{3+} in oc-

tahedral coordination, but the technique should be able to resolve tetrahedral Fe^{3+} (^{IV}Fe^{3+}) in ferrihydrite, particularly if it is present in amounts as much as 36% of the total iron, as was suggested by Eggleton and Fitzpatrick (1988). The aim of the present work was to record the Mössbauer spectrum for the 6-line ferrihydrite prepared by Eggleton and Fitzpatrick (1988) to a high level of resolution to determine whether Fe^{3+} substitution in tetrahedral sites of ferrihydrite was indicated. The χ^2 statistical test was used to differentiate between models containing doublets representing octahedral (^{VI}Fe^{3+}) and tetrahedral (^{IV}Fe^{3+}) structural components. The spectra were recorded to several different background counts to determine the effect this had on spectral resolution.

EXPERIMENTAL

Samples were synthesized by the method described by Eggleton and Fitzpatrick (1988) after Towe and Bradley (1967). The Mössbauer absorber was prepared by placing the sample diluted with powdered starch to give ~6 mg Fe/cm^2 into a Perspex piston-type holder. Mössbauer spectra were acquired in the constant acceleration mode into 512 channels (folded) with a ^{57}Co/Rh source. The velocity scale was calibrated with reference to iron metal foil, with the mid-point of the room temperature magnetic hyperfine iron spectrum defining zero velocity. The spectra were computer-fitted assuming Lorentzian lineshapes with the widths and dips of each pair of peaks constrained to be equal. A non-linear, least-squares regression χ^2 minimization procedure was used; convergence was achieved when a decrease in χ^2 value was no longer significant. The spectra were recorded for the same sample to background counts of 1, 2, and 3 $\times$ 10^6.

RESULTS

The ferrihydrite spectra recorded to different background counts were each computer-fitted to a number of models having combinations of one, two, three, or four doublets representing ^{IV}Fe^{3+} and ^{VI}Fe^{3+} components. No significant difference was found among the spectral parameters of the three spectra with different

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Table 1. Computer-fitted Mössbauer spectral parameters for ferrihydrite spectrum recorded to 3×10^6 counts.

Coord.	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	A (%)
$^{VI}Fe^{3+}$ model $\chi^2 = 1.59$				
VI	0.348 (1)	0.525 (11)	0.39 (1)	61 (5)
VI	0.342 (1)	0.854 (11)	0.33 (1)	28 (8)
VI	0.341 (2)	1.199 (33)	0.34 (2)	11 (4)
$^{IV}Fe^{3+} + {}^{VI}Fe^{3+}$ model $\chi^2 = 1.60$				
IV	0.190 (14)	0.726 (4)	0.41 (1)	25 (5)
VI	0.382 (6)	0.569 (6)	0.36 (1)	45 (5)
VI	0.401 (13)	0.886 (24)	0.39 (2)	30 (3)

background counts for any given model. The only significant difference between the fits was that the χ^2 value increased in a linear manner with increasing counts, as previously reported for nontronite (Johnston and Cardile, 1985).

$^{VI}Fe^{3+}$ model

The first model consisted of fitting doublets corresponding to $^{VI}Fe^{3+}$ sites; for example, the 3×10^6 background-count spectrum when fitted with one doublet gave $\chi^2 = 7.490$, two doublets gave $\chi^2 = 2.136$, and three doublets, $\chi^2 = 1.590$. Fitting a fourth $^{VI}Fe^{3+}$ doublet resulted in a small decrease in the χ^2 value, but more significantly, the error in the peak area was larger than the fitted component, indicating that no improvement in the fit had been achieved. Each additional fitted doublet had a greater Δ value and a relative spectral peak area smaller than the preceding doublet (Table 1).

$^{IV}Fe^{3+} + {}^{VI}Fe^{3+}$ model

Fitting doublets corresponding to one $^{IV}Fe^{3+}$ plus one $^{VI}Fe^{3+}$ resulted in $\chi^2 = 3.086$; one $^{IV}Fe^{3+}$ plus two $^{VI}Fe^{3+}$ doublets gave $\chi^2 = 1.602$ for the 3×10^6 background-count spectrum. Two $^{IV}Fe^{3+}$ doublets could not be fitted, nor could any other combination of $^{IV}Fe^{3+}$ and $^{VI}Fe^{3+}$ having more than three doublets, because the fitting procedure would not converge.

DISCUSSION

Based on the χ^2 values (Table 1) and a visual examination of the fitted spectra (Figure 1), little discernable difference exists between the model having three $^{VI}Fe^{3+}$ sites and the model having one $^{IV}Fe^{3+}$ and two $^{VI}Fe^{3+}$ sites. That the two different models gave such similar fits to the data is surprising. Although the model having the three $^{VI}Fe^{3+}$ doublets gave a slightly lower χ^2 value, this improvement may not be significant.

The $^{IV}Fe^{3+} + {}^{VI}Fe^{3+}$ Mössbauer model accounted for 25(5)% as $^{IV}Fe^{3+}$ (Table 1). If the assumption is made that the recoilless fraction for different sites in a mineral are equivalent, the Mössbauer analysis indicates a
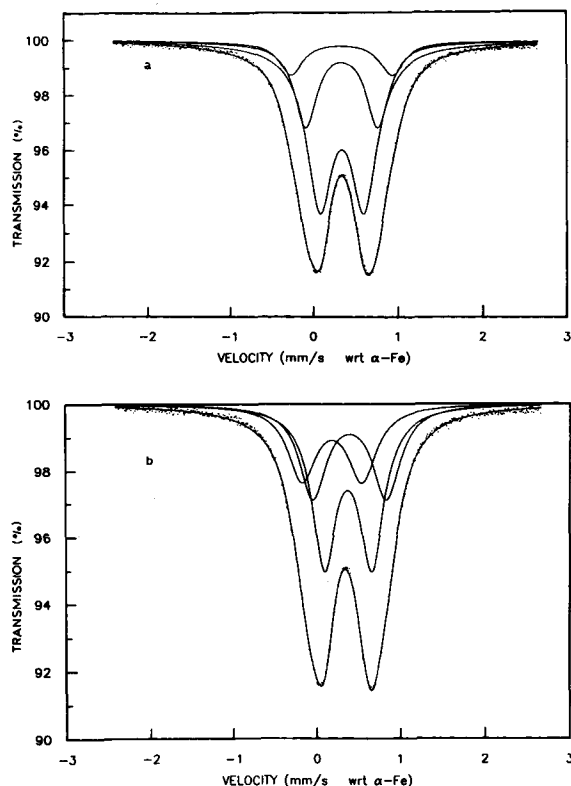

Figure 1. Experimental and computer-fitted Mössbauer spectrum for ferrihydrite recorded to 3×10^6 counts fitted with doublets corresponding to (a) three octahedral, and (b) one tetrahedral and two octahedral sites.

slightly lower site occupancy than the $\sim$36% $^{IV}Fe^{3+}$ proposed by Eggleton and Fitzpatrick (1988).

The present results support the concept that the fitted doublets do not represent discrete sites, but are a simplified representation of a continuum of distributions of Δ values arising from the varied environment surrounding Fe^{3+} within the ferrihydrite. These results indicate that Mössbauer spectral data cannot confidently differentiate between $^{IV}Fe^{3+}$ and $^{VI}Fe^{3+}$ in ferrihydrite nor demonstrate conclusively that $^{IV}Fe^{3+}$ was present in the sample studied.

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