STUDIES OF THE REACTIVITY OF THE FERRIHYDRITE SURFACE BY IRON ISOTOPIC EXCHANGE AND MÖSSBAUER SPECTROSCOPY

BRIGID A. REA,[1] JAMES A. DAVIS,[2] AND GLENN A. WAYCHUNAS[3]

[1] Water Resources Division, U. S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303

[2] Water Resources Division, U. S. Geological Survey, 345 Middlefield Rd., Menlo Park, California 94025

[3] Center for Materials Research, Stanford University, Stanford, California 94305

Abstract—Two-line ferrihydrite is an important adsorbent of many toxics in natural and anthropogenic systems; however, the specific structural sites responsible for the high adsorption capacity are not well understood. A combination of chemical and spectroscopic techniques have been employed in this study to gain further insight into the structural nature of sites at the ferrihydrite surface. The kinetics of iron isotopic exchange demonstrated that there are at least two types of iron sites in ferrihydrite. One population of sites, referred to as *labile* sites, approached iron isotopic equilibrium within 24 hr in ^{59}Fe–NTA solutions, while the second population of sites, referred to as *non-labile,* exhibited a much slower rate of isotopic exchange. Adsorbed arsenate reduced the degree of exchange by labile sites, indicating that the anion blocked or greatly inhibited the rate of exchange of these sites. Mössbauer spectra were collected from a variety of samples including ^{56}Fe-ferrihydrite samples with ^{57}Fe in labile sites, samples containing ^{57}Fe throughout the structure, and samples with ^{57}Fe in non-labile sites. The spectra showed characteristic broad doublets signifying poor structural order. Refined fits of the spectra indicated that labile sites have larger quadrupole splitting, hence more local distortion, than non-labile sites. In all cases, the spectra demonstrated some degree of asymmetry, indicating a distribution of Fe environments in ferrihydrite. Overall spectral findings, combined with recent EXAFS results (Waychunas *et al.,* 1993), indicate that labile sites likely are more reactive (with respect to iron isotopic exchange) because they have fewer neighboring Fe octahedra and are therefore bound less strongly to the ferrihydrite structure. The labile population of sites probably is composed of end sites of the dioctahedral chain structure of 2-line ferrihydrite, which is a subset of the entire population of surface sites. Mössbauer spectra of samples containing adsorbed arsenate indicated that the anion may slightly decrease the distortion of labile sites and stabilized the structure as a whole by bidentate bonding.

Key Words—Adsorption, Arsenate, Dissolution kinetics, Ferrihydrite, Iron octahedra, Mössbauer spectroscopy, Reactive sites, Solubility, Surface chemistry.

INTRODUCTION

The fate of dissolved ions in natural and anthropogenic systems is of great importance to water quality. Iron oxides and oxyhydroxides are particularly important in determining the fate of these ions because of their high surface area and ability to control adsorption and desorption processes (Schultz *et al.,* 1987). Ferrihydrite is a microcrystalline hydrous iron oxide that may exhibit a number of different crystalline phases (Towe and Bradley, 1967; Schwertmann and Fischer, 1973; Eggleton and Fitzpatrick, 1988; Manceau *et al.,* 1990). The least crystalline form of ferrihydrite, and presumably the most poorly ordered form, displays two broad X-ray diffraction peaks in the range 20°–90° 2θ with Cu radiation, which indicates poor structural order and small particle size (Schwertmann and Fischer, 1973; Murad and Schwertmann, 1980). This form of ferrihydrite, termed "two-line ferrihydrite" because of the X-ray diffraction pattern exhibited, has been found in association with ground water seeps from gold mine tailings (Fuller and Davis, 1989), with iron-bearing spring waters (Carlson and Schwertmann, 1981), and in soils from many locations (Childs and Johnston, 1980; Fitzpatrick, 1988). Two-line ferrihy-

drite also has been investigated for use as a metal adsorbent in the treatment of waste water containing high concentrations of metals (Schultz *et al.,* 1987; Leckie *et al.,* 1985). Ferrihydrites described herein are the two-line variety.

The widespread occurrence of ferrihydrite has prompted many studies of the mineral involving several types of spectroscopic and chemical techniques. In Waychunas *et al.* (1993), we discussed the structure of ferrihydrite, both in the presence and the absence of arsenate, based on Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The results of that study show that the elementary unit of the ferrihydrite structure is an Fe^{3+} ion surrounded by six close-packed O^{2-} or OH^- anions, i.e., an Fe octahedron. Larger units consist of the Fe octahedra joined by sharing edges, forming short double chains of Fe octahedra; these link further to other chains and pieces of chains by sharing corners to form a cross-linked structure similar to goethite or akaganeite (Figure 1). Electron micrographs usually indicate spherical crystal morphology (Schwertmann and Taylor, 1977) which Waychunas *et al.* (1993) suggest are large floccules or aggregates of the chained and cross-linked segments. Results from EXAFS spectroscopy (Waychunas *et al.,* 1993) further show
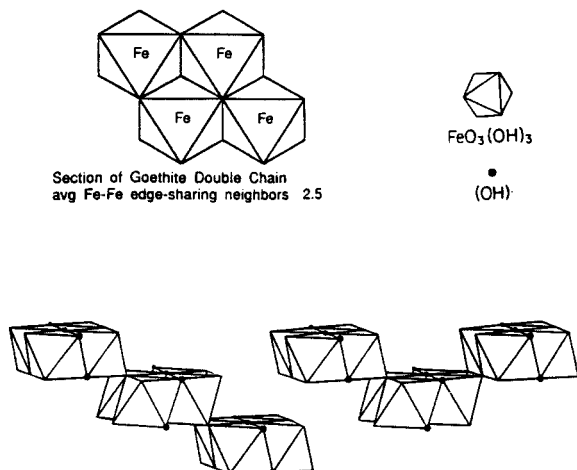
Figure 1. Schematic representation of two-line ferrihydrite structure. Top drawing shows plan view of linkages of iron octahedra to form short segment of dioctahedral chain. Bottom figure shows possible cross-linkages of dioctahedral chains.

that arsenate attaches to ferrihydrite as an inner-sphere complex, usually bonding to two adjacent Fe octahedra.

By assuming a structure for ferrihydrite similar to goethite or akaganeite, but lacking long-range order, we can infer that a fraction of the iron atoms should have lower than average coordination to other Fe octahedra, i.e., fewer Fe neighbors (e.g., Fe octahedra on the ends or edges of non-crosslinked dioctahedral chains, as in Waychunas *et al.,* 1993), and "interior" iron sites should have higher than average coordination than other Fe octahedra. In principle, iron sites with high Fe–Fe coordination should be more difficult to exchange, whereas iron octahedra with fewer neighbors should exchange more easily, that is, be more labile. This paper attempts to exploit the differences in Fe–Fe coordination to examine the surface reactivity of ferrihydrite. In theory, this experimental approach also could be applied to iron oxides with long-range structural order, e.g., goethite, although the proportion of sites with low Fe–Fe coordination relative to total Fe sites would be expected to be much smaller. The EXAFS results of Waychunas *et al.* (1993) provide an important framework for the application of Mössbauer and ^{59}Fe isotopic exchange findings; the latter techniques indicate differences between sites on the ferrihydrite that react quickly to isotopic exchange and those that exchange only slowly or not at all. The isotopic specificity of Mössbauer and ^{59}Fe isotopic exchange is especially useful for examining particular sites of interest on the ferrihydrite structure; the combination of chemical and spectroscopic techniques allows substantiation of the results from individual techniques.

The results from the iron isotopic exchange experiments coupled with the principles of isotopic equilib-

rium were used: 1) to determine the proportion of sites or Fe octahedra on ferrihydrite that are capable of exchanging rapidly with a dissolved Fe isotope, and 2) to develop a technique for isotopically enriching the surface of ferrihydrite for Mössbauer spectroscopic analysis. Arsenate was added in one of the exchange experiments to determine the effect of an adsorbed contaminant on the exchange process and the labile site measurement. Arsenate adsorption on ferrihydrite has been described by Waychunas *et al.* (1993) based on EXAFS spectroscopy. These authors found that the tetrahedral geometry of the adsorbed arsenate and As–O bond length does not alter from As(V) coordinated by water molecules in aqueous solutions. The size of the As tetrahedra and number of nearest neighbors show bidentate binuclear bonding to ferrihydrite. Although arsenate adsorption and Fe exchange are different processes, adding an adsorbing ligand in certain experiments may give insight into the differences in reactive sites and the mechanisms of crystal growth.

The structural characteristics of the reactive sites on ferrihydrite were determined through more direct measurements. Mössbauer spectroscopy provides information about the electron configuration and bonding environment around Fe nuclei in ferrihydrite. Because only one isotope of Fe can be detected by Mössbauer spectroscopy, specific portions of the ferrihydrite structure, such as the most reactive sites as determined by radioactive isotopic exchange, can be examined by selective enrichment with the Mössbauer-sensitive isotope. The addition of arsenate allows further investigation of the interactions between ferrihydrite and the anion through changes observed in the Mössbauer spectra.

METHODS

Synthesis

All ferrihydrite samples for this study were prepared in a similar manner; the concentrations of the solutions used for synthesis and aging times were variable. A general preparation technique will be given here with specific times and concentrations detailed in the following method subheadings.

Ferrihydrite suspensions were made from a solution of FeCl₃ and NaCl at low pH that was raised to pH 9 with NaOH while being stirred vigorously with a Teflon®-coated magnetic stir-bar*; the addition of NaOH took approximately 15 min. A fluffy, reddish-brown precipitate formed at pH near 4. The precipitate was allowed to age for a specified time with periodic ad-

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justments to the pH to maintain the value within 0.1 pH units of the desired value. No attempt was made to exclude CO_2 from any of the preparations.

Use of a complexing ligand for Fe(III) was necessary in these experiments to increase the concentration of total dissolved Fe(III). Without a complexing ligand, virtually all ^{59}Fe added to solution would be exchanged with the surface immediately because of the very low ratio of dissolved Fe to particulate Fe in the circum-neutral pH range. Under these conditions quantification of approach to isotopic equilibrium is essentially impossible experimentally. Both nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) were tried as complexing ligands. As will be seen below, both ligands yielded nearly the same results with respect to quantifying labile and non-labile site Fe populations. However, isotopic equilibrium with the labile sites was achieved more rapidly in NTA solutions, so this ligand was chosen in the preparation of samples for Mössbauer spectroscopy.

Before beginning the study of iron isotopic exchange, the rate and extent of ferrihydrite dissolution were determined in NTA and EDTA solutions. The rate of Fe dissolution of a ferrihydrite suspension (aged for 1 hr) in a 0.01 M NTA solution at pH 9 is shown in Figure 2. After 8 hr, a steady-state concentration of total dissolved iron (Fe_{diss}) equal to 0.74 mM was attained in 0.01 M NTA solution (Figure 2). HYDRAQL (Papelis et al., 1988) calculations indicate that the major dissolved Fe species in this solution are $Fe(NTA)_2^{3-}$ and $Fe(OH)_2NTA^{2-}$, using the thermodynamic data of Martell and Smith (1974). Assuming that these thermodynamic data are correct, the measured value of Fe_{diss} is consistent with a log K of -38.4 for the solubility product (expressed as $Fe(OH)_3$) for freshly precipitated 2-line ferrihydrite, which is within the range of values reported in the literature (Langmuir and Whittemore, 1971). In 0.03 M NTA solutions, an equilibrium concentration of 1.85 mM Fe_{diss} was observed. EDTA is a much stronger complexing ligand, and steady-state concentrations of Fe_{diss} were achieved within a few minutes of adding EDTA to a ferrihydrite suspension at pH 9. Speciation in the EDTA experiments is relatively simple; $Fe(OH)EDTA^{2-}$ is the only major dissolved Fe species and its concentration is equal to the molar concentration of EDTA added. For example, in the isotopic exchange experiment with EDTA, 0.6 mM total EDTA was added to the ferrihydrite suspension and Fe_{diss} was 0.6 mM (i.e., $Fe(OH)EDTA^{2-} = 0.6$ mM).

A large batch of goethite was prepared for experimentation following the method of Atkinson et al. (1968). $FeCl_3$ was hydrolyzed at pH 12 and aged in a polyethylene container at 60°C for 4.5 days. The precipitate was freeze-dried after removing salts by ultrafiltration. A portion of the goethite was rehydrated prior to experimentation.
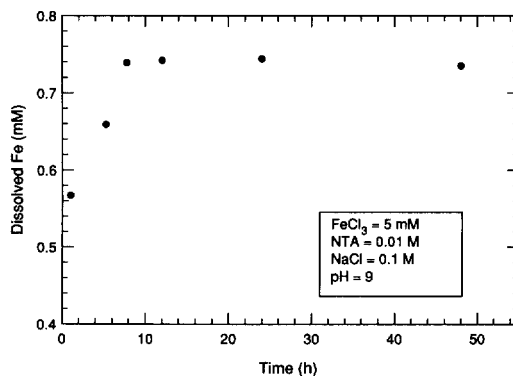

Figure 2. Kinetics of ferrihydrite dissolution at pH 9, in the presence of 0.01 M NTA and 0.1 M NaCl.

Iron-59 isotopic exchange

Iron-59 isotopic exchange experiments were performed in 2-liter glass beakers at 20 ± 3°C. Solution conditions were: Fe_{total} = 5 mM, NTA = 0.01 M or 0.03 M, NaCl = 0.1 M, and pH = 9.0 ± 0.1. One experiment was conducted with an EDTA concentration of 0.6 mM, following the procedure listed below with the EDTA taking the place of NTA.

The pH of an $FeCl_3$ and NaCl solution was raised to 9.0; the precipitate that formed was aged for 1 hr with continuous stirring. NTA (or EDTA) then was added to the suspension and the pH value was readjusted to 9.0 with NaOH; in one NTA experiment, the precipitate was aged for 6 days before adding the NTA. The ferrihydrite suspension was allowed to age for 24 hr, whereupon a 25 ml aliquot was removed and centrifuged at 30,500 g for 30 min. An aliquot of the supernatant solution was decanted carefully and a small volume (0.1 ml) of ^{59}Fe labeled $FeCl_3$ solution in 0.1 M HCl (received from New England Nuclear Research Products, Boston, Massachusetts, as [59]$FeCl_3$) was added to the decanted solution; a molar equivalent of NaOH was added to maintain the pH value at 9.0. The aliquot of ^{59}Fe solution added only 1.3 μM stable Fe and 0.5 nM ^{59}Fe to the supernatant, thus the Fe-NTA solution speciation in the supernatant was minimally disturbed by the aliquot addition and the ^{59}Fe was present at a concentration many orders of magnitude less than stable Fe isotopes. After equilibrating for 1 hr, the supernatant solution containing ^{59}Fe was returned to the 2-liter beaker containing the balance of the suspension. This step in the procedure allowed the added [59]Fe_{diss} to achieve the same speciation as Fe_{diss} in the supernatant solution before isotopic exchange with the precipitate began. Approaching the same speciation for ^{59}Fe in NTA solutions was assured by the excess of NTA in solution over Fe_{diss}.

The first sampling of supernatant took place after 5 min of mixing the suspension. Sampling was per-

Table 1. Description of samples for Mössbauer spectroscopy.

Sample	Description
MF5	^{56}Fe-ferrihydrite exchanged for 24 hr with $^{57}FeCl_3$ (^{57}Fe in labile sites)
MF6	^{56}Fe-ferrihydrite exchanged for 20 min with $^{57}FeCl_3$ (^{57}Fe in most reactive labile sites)
MF7	Ferrihydrite prepared with natural abundance of Fe isotopes throughout structure (^{57}Fe in bulk sites)
MF8	Ferrihydrite prepared with natural abundance of Fe isotopes, then exchanged three times for 24 hr with $^{56}FeCl$ (^{57}Fe in non-labile sites, i.e., least reactive sites)
MF9	^{56}Fe-ferrihydrite containing adsorbed arsenate exchanged for 24 hr with $^{57}FeCl_3$
MF10a	^{56}Fe-ferrihydrite exchanged for 24 hr with ^{57}Fe, then 20 min with Na_2HAsO_4
MF10b	^{56}Fe-ferrihydrite exchanged for 24 hr with ^{57}Fe, then 72 hr with Na_2HAsO_4

formed by removing two 25 ml aliquots of suspension, which were centrifuged at 30,500 g for 50 min; 5 ml of the supernatant solution was collected for $^{59}Fe_{diss}$ analysis. Another 5 ml aliquot of the uncentrifuged suspension was removed to determine the total ^{59}Fe activity. The samples were analyzed for ^{59}Fe by gamma spectrometry with either a Packard Minaxi Gamma or a Beckman Gamma 8000 gamma counter. Additional samples were taken at 2, 4, 8, 12, and 24 hr and then twice a day for the next week. The pH was maintained at 9.0 ± 0.1 during this time by periodic addition of 0.1 M NaOH.

To measure Fe isotopic exchange in the presence of arsenate, a single experiment was conducted where an aliquot of Na_2HAsO_4 solution (yielding $[AsO_4^{-3}]_{Total}$ $= 1 \times 10^{-3} M$) was added to the suspension 2 hr after the Fe precipitate formed, and 1 hr after NTA addition (23 hr before ^{59}Fe addition).

For the goethite isotopic exchange experiment, 100 g of freeze-dried goethite was rehydrated in 1 liter of 0.1 M NaCl at pH 2.5. After 1 hr, $FeCl_3$ was added to the suspension to hasten equilibration to a constant Fe_{diss} concentration at that pH; this suspension was aged for 24 hr before beginning the isotopic exchange. Addition of ^{59}Fe and sampling followed the procedure listed above.

Mössbauer spectroscopy

Using the methods and results of the ^{59}Fe isotopic exchange experiments, Mössbauer spectroscopy samples were prepared with ^{57}Fe ions placed in specific sites of the ferrihydrite structure. Mössbauer spectroscopy detects exclusively ^{57}Fe among all other iron isotopes; therefore, pure ^{56}Fe ferrihydrite samples were prepared and later enriched with ^{57}Fe for examination of Fe sites that exchange readily with solution. Other samples were prepared with ^{57}Fe in sites that did not readily exchange, and with ^{57}Fe in natural abundance in sites throughout the ferrihydrite structure. The ^{56}Fe isotope was obtained as $^{56}Fe_2O_3$ from Oak Ridge National Laboratory, Oak Ridge, Tennessee (99.87 atomic percent ^{56}Fe, 0.07 atomic percent ^{57}Fe, and 0.05 atomic percent ^{54}Fe); a portion of the iron oxide was dissolved in 6 N HCl over low heat to form a 0.22 M $^{56}FeCl_3$ solution. The ^{57}Fe isotope was received as iron

metal from Isotec Inc., Miamisburg, Ohio (95.81 atomic percent ^{57}Fe, 3.53 atomic percent ^{58}Fe, and 0.66 atomic percent ^{56}Fe); the metal was dissolved completely in warm, concentrated HCl, forming a 0.072 M $^{56}FeCl_3$ solution. Both solutions were stored at a pH value less than 1.0 in tightly sealed plastic bottles. Descriptions of each Mössbauer sample preparation follow below and Table 1 summarizes the preparations. Single samples were made for each spectrum; all samples were prepared at room temperature.

Samples MF5 and MF6. In a small glass beaker with a Teflon®-coated stir bar, 0.91 ml of the $^{56}FeCl_3$ stock solution in 25 ml of H_2O was titrated with NaOH to pH 9. After aging the precipitate for 1 hr, 4 ml of 0.1 M NTA was added and the volume adjusted to 40 ml. The sample then was aged at room temperature for 1 day with constant stirring. The pH value of the suspension was maintained at 9.0 by periodic manual adjustment.

The aged, pure ^{56}Fe ferrihydrite sample was centrifuged at 16,000 g for 10 min; the supernatant solution was decanted and discarded. Sonication in 8 ml of 0.03 M NaCl solution was used to resuspend the residual pellet, until the solution appeared homogeneous (i.e., no large particles were visible to the eye). A new supernatant solution was prepared, to replace the original solution and to introduce the ^{57}Fe for exchange, consisting of: 0.39 ml of $^{57}FeCl_3$ stock solution (to give a final Fe_{diss} concentration of 0.74 mM, consistent with the value determined during ferrihydrite dissolution at pH 9 in 0.01 M NTA solution, see Synthesis above), 4 ml of 0.1 M NTA, and 10.4 ml of 0.03 M NaCl. The pH of the new supernatant solution was adjusted to 9.0 with NaOH, and the solution was added to the resuspended ferrihydrite particles, thereby reproducing synthetically the conditions in the sample solution before centrifugation (0.1 M NaCl, 0.74 mM Fe_{diss} and 0.01 mM NTA). The resuspended material was allowed to equilibrate with the new supernatant solution: 1) for 20 min to study sites where very fast isotopic exchange occurred (sample MF6), or 2) for 24 hr to study the labile sites, i.e., defined as those sites which exchanged isotopically in 24 hr in NTA solutions (sample MF5).

Samples MF7 and MF8. Using the exchange technique described above, the supernatant solution of a ferrihydrite sample containing the natural abundance of iron isotopes (prepared from Baker reagent grade $FeCl_3 \cdot 6H_2O$) was exchanged three times (ca. 24 hr each time) with an ^{56}Fe-rich solution to produce a sample with the labile sites depleted in ^{57}Fe (sample MF8). Mössbauer spectroscopy on this sample would detect only iron sites that were not exchanged easily. These sites will be referred to as *non-labile sites* in this work. A reference ferrihydrite, with the same proportion of ^{57}Fe in all iron sites, *bulk sites,* was prepared using Baker $FeCl_3 \cdot 6H_2O$ reagent containing the natural abundance of iron isotopes (sample MF7).

Samples MF9, MF10a, and MF10b. When arsenate was included in the sample suspensions, 0.8 ml of a 0.05 M Na_2HAsO_4 solution was added before the 1-day aging period, but 1 hr after the NTA was added (sample MF9); or Na_2HAsO_4 was added after surface enrichment with ^{57}Fe for 24 hr. In the latter case, two samples were prepared: one that reacted with the arsenate for 20 min (sample MF10a) and one that reacted for 72 hr (sample MF10b). This change in reaction time was used to obtain samples with varying As adsorption; however, arsenate coverage probably did not increase greatly from the 20 min sample to the 72 hr sample (Fuller *et al.,* 1993).

After each sample suspension had been exchanged for the prescribed amount of time, the suspensions were divided into eight equal portions. Each portion was filtered onto a separate 0.45 μm Millipore filter; the ferrihydrite precipitate was retained on the filter paper. A silicone gasket was inserted into the filtering apparatus to concentrate the sample onto a 2.5-cm diameter circular area. The filtered fractions were air-dried flat at room temperature overnight (ca. 12 hr). In the sample holder of the Mössbauer spectrometer, the eight filter papers were stacked, mounted vertically, and secured in place by a metal O-ring and four bolts. This stacking technique was used to produce a homogeneous sample without pinholes or cracks, thereby reducing the chance of unattenuated radiation reaching the detector.

The instrument used for Mössbauer spectroscopy, located in the Center for Materials Research at Stanford University, consisted of a palladium-matrix ^{57}Co gamma source mounted on a constant acceleration vibrator. Mössbauer spectra were collected in transmission. Sample absorption varied between 0.5% and 5.0%. A single Mössbauer spectrum was collected for each sample at room temperature (ca. 25°C). Mirrored spectra, collected in 512 channels of a multichannel analyzer between a source velocity of 3.5 and -3.5 mm s^{-1} were folded and normalized for comparison. A spectrum was considered complete when the signal-to-noise ratio did not improve significantly with time. In most cases this dictated that counts were accumulated until the baseline (i.e., the channels where no resonant absorption occurred) was approximately 2×10^6 counts per channel. A baseline of 4×10^6 counts per channel or more was desirable in samples with a low ^{57}Fe content.

Iron foil and an iron oxalate/sodium nitroprusside mixture were used for spectral velocity calibration. Isomer shift (IS) calibration was accomplished by fitting the centroid peak positions of the above materials (10 peaks) to a third order polynomial. Estimated 2 sigma errors in IS are 0.03 mm s^{-1}. All isomer shift values are reported relative to iron foil.

For data analysis, the Mössbauer spectra were fit first with a single Lorentzian doublet. Peak parameters and background values determined in the single-doublet fit were used to approximate two-doublet values for further refinement. Ideally, each Lorentzian doublet fit to each spectrum would represent a particular Fe environment. In the case of ferrihydrite, a broad distribution of doublets should be needed to fit the spectra perfectly because of the supposed range of iron sites; therefore, the two-doublet fit is only an approximation (cf. Murad and Johnston, 1987). Two-Lorentzian-doublet fits have been found to be adequate in most ferrihydrite studies because the index of fitting error (either χ^2 or MISFIT) does not improve significantly with additional Lorentzian doublets (Cardile, 1988); two doublet fits were, therefore, used in this study. The two doublets should not be interpreted to represent two distinct Fe sites in ferrihydrite, although the fits can be used to probe qualitative differences in Fe environments. In all spectral fits, the line shape was constrained to have 100% Lorentzian character and the areas of the peaks in each doublet were constrained to be equal. All constraints should have been lifted for a final fitting; however, the fitting program either would not converge or gave errors, such as negative peak areas, when all constraints were lifted. Mössbauer theory dictates that Fe(III) in randomly oriented samples gives rise to areas in component doublet peaks that are equal (Bancroft, 1973); thus equal-area constraints for Fe(III) samples were used in the present study. No baseline correction was employed in the fitting program, since assumptions about baseline shape are difficult to make without prior experience with a sample. Folding the Mössbauer spectra should eliminate the sinusoidal background effect that results from the oscillating source to detector distance (Waychunas, 1979). The parameters, MISFIT and ΔMISFIT (Ruby, 1973), were used to determine the goodness-of-fit on the suite of spectra. Although similar to the χ^2 statistic, MISFIT does not depend as strongly on data quality or background count level. Both parameters are used in the Mössbauer literature with MISFIT gaining popularity in recent years (Hawthorne and Waychunas, 1988). A complete description and comparison of MISFIT with
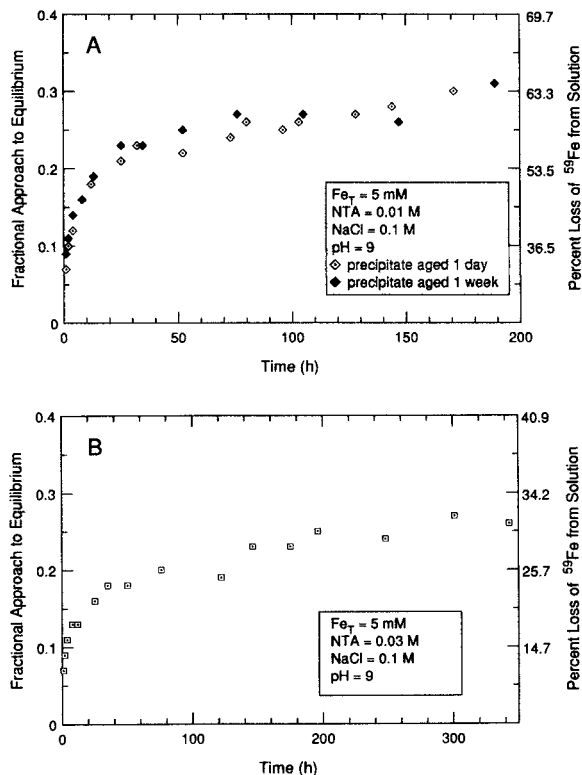
Figure 3. Iron isotopic exchange A) with ferrihydrite, centered and filled diamonds, in presence of 0.01 M NTA, ferrihydrite aged 1 day and 1 week, respectively; and B) with ferrihydrite in presence of 0.03 M NTA, ferrihydrite aged 1 day.

χ^2 has been given by Ruby (1973), Waychunas (1979), Hawthorne and Waychunas (1988), and Hawthorne (1988).

RESULTS

Exchange studies

Kinetic data for iron isotopic exchange of ferrihydrite in NTA solutions are shown in Figure 3. Relatively fast loss of ^{59}Fe from solution occurred during the first 24 hr compared with ^{59}Fe loss after that time. The rate of ^{59}Fe loss from solution was independent of whether the ferrihydrite was aged for 1 day or 1 week before addition of the ^{59}Fe (Figure 3A). At isotopic equilibrium, the ratio of the concentration of ^{59}Fe isotope to that of total iron isotopes in the dissolved phase should be the same as that in the precipitate, i.e.,

$$\frac{^{59}Fe_{diss}}{Fe_{diss}} = \frac{^{59}Fe_{part}}{Fe_{part}} \qquad (1)$$

where Fe_{diss} refers to the concentration of total dissolved iron and Fe_{part} refers to the total iron in ferrihydrite particles. The percent of ^{59}Fe lost from solution
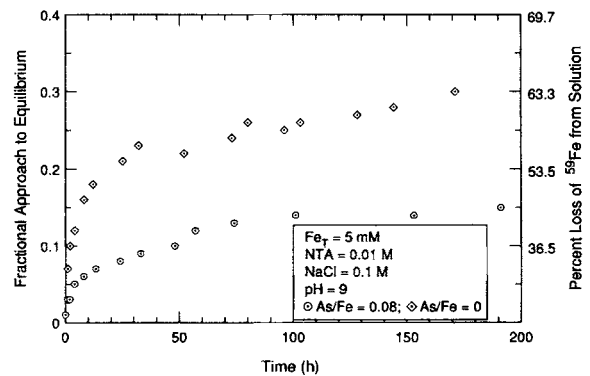

Figure 4. Iron isotopic exchange with ferrihydrite, centered diamonds, in presence of 0.01 M NTA, ferrihydrite aged 1 day; centered circles, in presence of 0.01 M NTA and 1 mM arsenate, ferrihydrite aged 1 day.

at complete isotopic equilibrium can be calculated as follows:

$$\% \ ^{59}Fe \ lost = \frac{^{59}Fe_{part}}{^{59}Fe_{diss} + \ ^{59}Fe_{part}} = \frac{Fe_{part}}{Fe_{diss} + Fe_{part}} \qquad (2)$$

The values of Fe_{diss} and Fe_{part} are dependent on the conditions used in each system. For example, in 0.01 M NTA solution, $Fe_{diss} = 0.74$ mM, $Fe_{part} = 4.26$ mM, and the % ^{59}Fe lost from solution at complete isotopic equilibrium would be 85.2%. After the initial 24 hr uptake period in 0.01 M NTA solution (Figure 3A), slower removal of ^{59}Fe from solution occurred through the end of the experiment (approximately 200 hr), even though the ferrihydrite was still far from reaching isotopic equilibrium with the aqueous phase. Changing the NTA concentration to 0.03 M increased the value of Fe_{diss} that was in equilibrium with the ferrihydrite suspension (see methods). Under these conditions, the percentage of ^{59}Fe removed from solution during isotopic exchange decreased as expected (Figure 3B). The fractional approach toward isotopic equilibrium, however, was nearly the same, and decreased to a slow rate well before isotopic equilibrium was achieved. Addition of arsenate (as Na_2HAsO_4) to the system significantly decreased the loss of ^{59}Fe from solution (Figure 4, centered circles) compared with the experiment with no arsenate (Figure 4, centered diamonds). Arsenate adsorption on the ferrihydrite in this system yielded an As/Fe molar ratio of 0.08 in the precipitate, about 32% of the maximum adsorption measured under these conditions (Fuller *et al.*, 1993).

The isotopic exchange experiments with EDTA yielded a different shaped curve of fractional approach to equilibrium (Figure 5). The transition from a fast rate of exchange to a slower rate was less distinct and occurred over a longer period of time (approximately 48 hr) than was observed in NTA solutions.

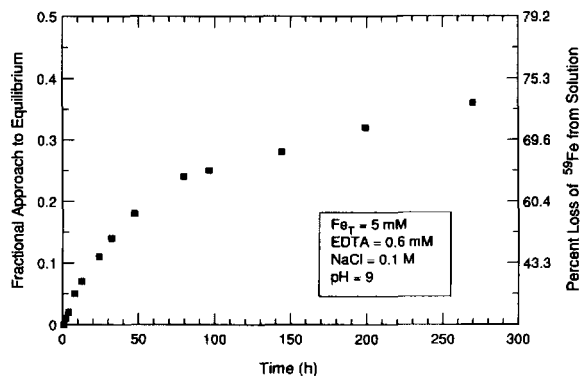Iron isotopic exchange also was attempted with goe-

Figure 5. Iron isotopic exchange with ferrihydrite in presence of 0.6 mM EDTA; ferrihydrite aged 1 day.

Figure 6. Mössbauer spectra of ferrihydrite samples at 25°C. "•" denote observed data points; solid line traces two-doublet fit of Mössbauer spectra. See text for explanation of each sample.

thite, a well-crystallized hydrous iron oxide. Unfortunately, the method was not well suited to this application. Establishing that dissolution equilibrium was reached in NTA solutions before beginning the exchange reaction was difficult, and very little loss of ^{59}Fe from solution was observed during 200 hr of exchange. The results suggest that the rates of the forward and backward reactions that maintain goethite solubility at equilibrium are too slow to use isotopic exchange as an investigative method.

Mössbauer spectroscopy

Mössbauer spectra are shown in Figure 6. The "•" symbols denote observed data points and the solid-line traces are the computer-fit envelope. The envelope is the sum of the two Lorentzian doublets used to fit the data.

All spectra displayed only paramagnetic doublets. Many researchers (Murad and Schwertmann, 1980; Childs and Johnston, 1980; Johnston and Lewis, 1983; Cardile, 1988; Murad, 1988) have reported similar doublets for both natural and synthetic ferrihydrite samples. No magnetically split hyperfine component lines are observed because of the small particle size of the ferrihydrite and its correspondingly low magnetic ordering temperature, in the range 115–25 K depending on crystallite size (Murad and Johnston, 1987; Murad *et al.,* 1988). A number of the spectra displayed asymmetry (i.e., the low velocity peak of the doublet had a larger intensity than the high-velocity peak, see Figure 6).

Isomer shift (IS) values derived from fitting the spectra ranged from 0.31 to 0.38 mm s^{-1}, relative to Fe foil (Table 2). The IS values for Fe(III) and Fe(II) generally fall between 0.24–0.54 mm s^{-1} and 0.74–1.24 mm s^{-1}, respectively (Bancroft, 1973). Therefore, the values for IS in Table 2 are consistent with Fe(III).

In addition to information about the oxidation state, IS often can be used to characterize the coordination of ^{57}Fe. Trivalent iron is generally found in either six-
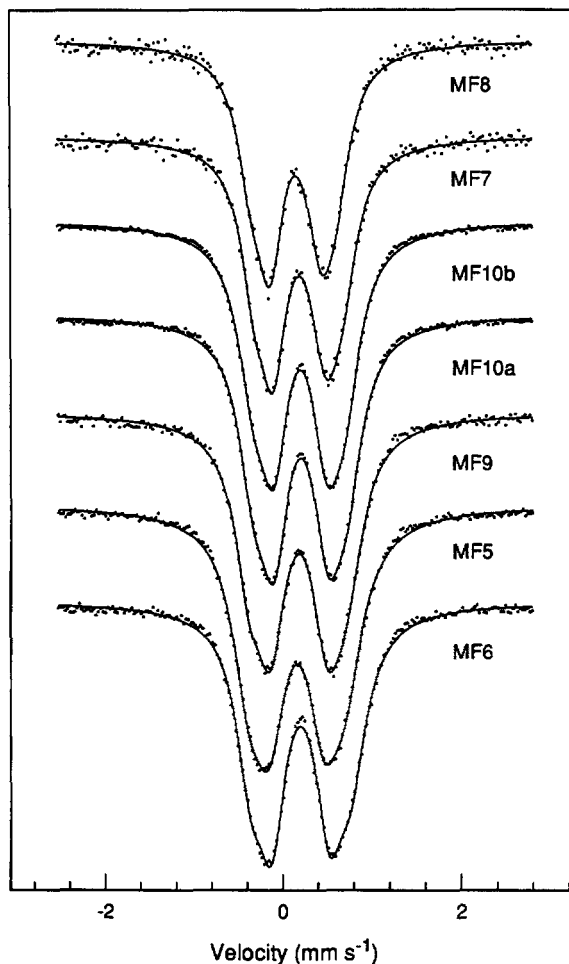
or fourfold Fe–O coordination, corresponding to IS ranges of 0.34 to 0.54 mm s^{-1} and 0.24 to 0.44 mm s^{-1}, respectively (Bancroft, 1973). Since the IS values in Table 2 fall within both ranges, the spectral data did not provide enough information to determine whether the ^{57}Fe was octahedrally (sixfold) or tetrahedrally (fourfold) coordinated. Cardile (1988) confirmed the difficulty of determining Fe–O coordination by fitting a ferrihydrite Mössbauer spectrum with model spectra consisting of either all octahedral Fe(III) or a 2:1 combination of octahedral:tetrahedral Fe(III) sites. The author found equal success with both fits and concluded that the coordination of ^{57}Fe in ferrihydrite could not be determined conclusively by room temperature Mössbauer spectra. X-ray absorption spectroscopy studies (EXAFS and X-ray absorption near edge structure (XANES)) conclusively have shown Fe–O octa-

Table 2.   Computer fitted Mössbauer parameters of two-line ferrihydrite samples.

Sample	IS (mm s^{-1})	QS (mm s^{-1})	Percent area	MQS (mm s^{-1})*
MF8	0.31 (3)	0.97 (3)	29 (8)	0.69 (4)
	0.33 (2)	0.58 (2)	71 (8)	
MF7	0.36 (2)	1.02 (2)	27 (6)	0.71 (3)
	0.37 (1)	0.60 (1)	73 (6)	
MF10b	0.37 (1)	1.04 (1)	40 (3)	0.78 (2)
	0.38 (1)	0.60 (1)	60 (3)	
MF10a	0.37 (1)	1.06 (1)	40 (3)	0.79 (2)
	0.38 (1)	0.61 (1)	60 (3)	
MF9	0.35 (1)	1.11 (1)	37 (4)	0.81 (2)
	0.36 (1)	0.64 (1)	63 (4)	
MF5	0.34 (1)	1.10 (1)	41 (4)	0.82 (2)
	0.33 (1)	0.62 (1)	59 (4)	
MF6	0.38 (1)	1.13 (1)	45 (3)	0.87 (2)
	0.38 (1)	0.65 (1)	55 (3)	

Values in parentheses indicate error in the last significant figure.
* MQS = mean quadrupole splitting, the sum of the products of the individual QS values and their respective areas.

hedral coordination for Fe gels and for ferrihydrite (Waychunas *et al.*, 1993; Manceau *et al.*, 1990; Combes *et al.*, 1989); sixfold coordination, therefore, has been assumed for this study.

Quadrupole splitting (QS) values give information concerning the local molecular environment of an ^{57}Fe atom. The arrangement of bonding ligands and electron configuration influence QS in such a way that distortion from a regular, perfect octahedral site is observable. In the case of Fe(III), an increase in QS indicates a higher degree of distortion relative to a perfect octahedral ligand field. "Distortion" here refers to the geometric arrangement of chemical bonds around the ^{57}Fe ion. This Mössbauer parameter will be used to demonstrate differences between labile and non-labile iron sites, and to examine the effect of adsorbed AsO_4^{-3} ligands on the labile Fe octahedra. Table 2 shows QS values determined in this study and Table 3 shows those from a number of other studies. To simplify comparison between samples, mean quadrupole splitting (MQS) values were calculated and are used in the following text. The MQS value is the sum of the products of the individual QS values and their respective areas (Waychunas, 1979); MQS values also were calculated from the QS and area values of other researchers when both parameters were available. MQS values are listed in Tables 2 and 3.
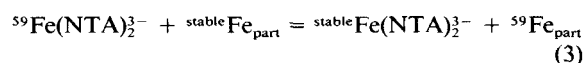
DISCUSSION

Description of Fe sites of the labile fraction

In 0.01 M NTA solution the exchange of iron isotopes progressed about 20% toward isotopic equilibrium in the first 20 hr, and then the approach toward equilibrium slowed very significantly (Figure 3A). If all iron sites were equally accessible, the rate of isotopic exchange would not decrease substantially until the

sites were nearly saturated, e.g., at a fractional approach to equilibrium greater than 0.7 (see, for example, Crank, 1975). Thus, the data suggest that at least two different rate-determining processes control the reaction progress toward iron isotopic equilibrium. In the simplest models, the data for this set of conditions could be described either by two types of iron sites in the structure or by two different rate-determining mechanisms in a one-site model. In 0.03 M NTA solution and EDTA solutions, the transition between the two different processes was more gradual than in 0.01 M NTA solution, suggesting that the rate-determining mechanisms may not be the same under each set of conditions. However, except in the presence of arsenate, the fractional approach to equilibrium slowed considerably above a value of 0.2 under all conditions studied (Figures 3–5). This suggests that a two-site model, which we have referred to in the general terms of labile and non-labile sites, is an appropriate model. Moreover, as will be discussed below, the Mössbauer spectroscopic results confirm that the bonding characteristics of labile and non-labile sites are different.

The iron isotopic exchange reactions in NTA solutions are written in terms of exchange between solution species and particles, e.g.,

$$^{59}\text{Fe(NTA)}_2^{3-} + {}^{\text{stable}}\text{Fe}_{\text{part}} = {}^{\text{stable}}\text{Fe(NTA)}_2^{3-} + {}^{59}\text{Fe}_{\text{part}} \tag{3}$$

Presumably, the initial, faster process in NTA solutions involves an exchange of iron atoms in octahedra that have the lowest Fe–Fe coordination (i.e., sites on the ends and edges of ferrihydrite particles; see Figure 1). The strong inflection point in the exchange rate approach to equilibrium (Figure 3A) suggests that this population of labile sites achieves isotopic equilibrium with the solution phase near the point that the fractional approach to equilibrium is 0.2. Extrapolation of a regression fit of the data representing the slow process (data for time >50 hours) back to zero time yields values of 0.17, 0.19, and 0.21 at the intercept (0.03 M NTA, 0.6 mM EDTA, and 0.01 M NTA solutions, respectively) for the fractional approach to isotopic equilibrium. The average value of these intercepts (0.19) implies that the labile sites represent 19% of the total iron in the precipitate.

Based on our EXAFS study of ferrihydrite structure and of arsenate adsorption and coprecipitation (Waychunas *et al.*, 1993; Fuller *et al.*, 1993), it is possible to examine why 19% of the iron octahedra might comprise the labile population. Consider a small hypothetical ferrihydrite particle, similar to those shown in Figure 1, but with longer dioctahedral chains; a number of Fe octahedra with various Fe–Fe coordination values are visible. Iron octahedra at the end of chains can have as little as two nearest Fe neighbors and as many as three; Fe octahedra at edge sites typically have 4 Fe

Table 3. Computer fitted Mössbauer parameters of other researchers.

Sample	IS (mm s⁻¹)	QS (mm s⁻¹)	Percent area	MQS (mm s⁻¹)[1]	XRD lines
$^{VI}Fe^{3+}$ model[2]	0.341 (2)	1.199 (33)	11 (4)	0.691 (87)	6
	0.342 (1)	0.854 (11)	28 (8)		
	0.348 (1)	0.525 (11)	61 (5)		
10 min[3]	0.35 (1)	0.83 (1)	53 (4)	0.68 (2)	6
	0.36 (1)	0.50 (1)	48 (4)		
30 min[3]	0.34 (1)	0.84 (1)	51 (2)	0.67 (1)	6+
	0.36 (1)	0.50 (1)	49 (2)		
LC31[4]	0.348 (1)	0.90 (1)	56 (3)	0.75 (4)	6
	0.353 (1)	0.550 (6)	44 (3)		
N163[4]	0.351 (1)	0.940 (4)	55 (1)	0.77 (3)	6
	0.352 (1)	0.573 (2)	45 (1)		
LC2[4]	0.349 (1)	0.99 (1)	66 (4)	0.86 (2)	2
	0.355 (1)	0.618 (9)	34 (4)		
PF[5]	0.33 (1)	0.99 (1)	42 (5)	0.76 (2)	2
	0.34 (1)	0.60 (1)	58 (6)		
2[6]	0.35 (1)	0.90 (2)	*		2
	0.36 (1)	0.52 (1)			
13/0[6]	0.33 (1)	0.87 (2)	*		2
	0.34 (1)	0.54 (2)			

Values in parentheses indicate error in the last significant figure.

[1] MQS = mean quadrupole splitting, the sum of the products of the individual QS values and their respective areas.

[2] Six-line ferrihydrite fit with all octahedral Fe^{3+} (Cardile, 1988).

[3] Six-line ferrihydrite heated for 10 and 30 min. Mössbauer spectra exhibited no hematite structure (Johnston and Lewis, 1983).

[4] N163, LC31 = "Relatively well-crystallized ferrihydrite"; LC2 = "Extremely poorly-crystallized ferrihydrite" (Murad *et al.,* 1988).

[5] "Proto-ferrihydrite" (Childs and Johnston, 1980).

[6] Sample 2 = naturally occurring two-line ferrihydrite; sample 13/0 = synthetic two-line ferrihydrite (Murad and Schwertmann, 1980).

* No areas reported; no MQS could be calculated.

neighbors, and if the chains cross-link (i.e., share corners), Fe octahedra at cross-linked sites have Fe–Fe coordination greater than 4, up to as many as 8. Postulating that the end sites with an Fe–Fe coordination of two are the most labile sites and that the *average* dioctahedral chain contains 20 octahedra (i.e., 4 end sites per 20 Fe octahedra) yields a labile population of sites that is 20% of total Fe sites.

As mentioned above, cross-linking of dioctahedral chains increases the number of nearest iron neighbors for end sites. However, cross-linking may not greatly influence the lability of the end sites. Evidence for this can be seen from the effects of one week of aging of 2-line ferrihydrite, which: 1) increases the degree of cross-linking of particles (Waychunas *et al.,* 1993); 2) decreases the adsorption of arsenate, due to a loss of surface sites caused by cross-linking (Fuller *et al.,* 1993); and 3) has no discernible effect on the approach to isotopic equilibrium for the labile fraction (Figure 3A). The results suggest that the population of sites in the labile fraction does not simply represent all surface sites that may adsorb ions. For example, arsenate forms both bidentate, binuclear bonds (one arsenate ion bonded to two Fe octahedra) and mononuclear, monodentate bonds at the ferrihydrite surface (Waychunas *et al.,* 1993). This would occur most commonly on the edges of the dioctahedral chains, but also would in-

volve a certain portion of the end sites. The edge site bonding would usually involve Fe octahedra that have a higher Fe–Fe coordination than end sites, and these octahedra would be expected to be included in the non-labile fraction with respect to iron isotopic exchange. On the other hand, some end sites of the labile fraction must be blocked by arsenate adsorption, since the approach to iron isotopic equilibrium was affected by arsenate adsorption (Figure 4). In that experiment, arsenate adsorption was about 32% of the maximum (Fuller *et al.,* 1993), and the population of labile Fe sites appears to have been reduced by about 50% (Figure 4). Although the labile fraction may not include all surface sites, it may instead be a good representation of the population of sites that are involved in maintaining the solubility of the phase via dissolution and reprecipitation reactions.

Mössbauer spectroscopy of the labile and non-labile sites

Sample MF8 (^{57}Fe in non-labile sites) had the lowest MQS value, 0.69(4) mm s⁻¹, indicating an average value of the least distorted sites in ferrihydrite. Sample MF7 (^{57}Fe representing all sites, referred to here as bulk sites) had a MQS value that was not significantly different from MF8 at 0.71(3) mm s⁻¹ indicating that the bulk of ferrihydrite consists of predominantly non-

labile sites. Both samples MF8 and MF7 show similar MQS values to the six-line ferrihydrite samples studied by Cardile (1988) and Johnston and Lewis (1983), but the MQS values differ from the six-line ferrihydrite samples of Murad *et al.* (1988) and the two-line ferrihydrite samples of Childs and Johnston (1980) and Murad *et al.* (1983) (cf. table 3). These differences point out a problem in trying to compare samples between studies because of differences in sample preparation and the way in which samples are described by researchers. For example, both LC2 (Murad *et al.*, 1988) and PF (Childs and Johnston, 1980) were described as two-line ferrihydrite very poorly crystallized, and yet give MQS values that are very different. Observed changes within a particular study are likely to be more credible since differences due to sample preparation and instrumentation are minimal.

Samples MF8 and MF6 (^{57}Fe in the most readily exchangeable labile sites) showed the greatest difference in MQS values, 0.69(4) mm s^{-1} *vs.* 0.87(2) mm s^{-1}, respectively. The higher MQS in sample MF6 suggests more distortion in the labile sites. Decreased bond strength and longer bond lengths of the labile ions (as indicated by IS values) are possible distorting effects. Sample MF5 (^{57}Fe in labile sites) showed a higher MQS value, 0.82(2) mm s^{-1} relative to sample MF8 as well. Murad *et al.* (1988) reported a similar correlation between higher QS and higher octahedral site distortion that was observable even with single-doublet fits to Mössbauer spectra.

Comparison of the MQS values of samples MF5 and MF6 leads to information on the characteristics of labile sites, including insight into their exchange kinetics. Samples MF5 and MF6 are similar in that they both have labile sites enriched with ^{57}Fe, but sample MF5 stayed in suspension with the isotopically enriched solution for a longer time period (24 hr *vs.* 20 min for sample MF6). Consequently, MF5 should contain all the sites found in MF6 plus additional sites from the longer reaction time. The difference in MQS values between MF5 and MF6 indicates that the labile sites that exchange more slowly (those that exchange after the first 20 min) are less distorted and contribute to lowering the MQS for sample MF5 relative to MF6. Thus, the Mössbauer MQS values indicate that labile Fe sites that exchange rapidly (within 20 min) are different from those that exchange during the first 24 hr; specifically, the most reactive labile sites are the most distorted.

From the Mössbauer spectroscopy MQS values, it is evident that the labile sites are on average the most distorted sites. The labile sites evidently are not bound to the structure as strongly as the non-labile sites which explains the ease with which Fe exchanges and the more rapid exchange as observed in the ^{59}Fe isotopic exchange experiments. The less distorted sites, as determined by Mössbauer spectroscopy, are non-labile

sites. These sites may be stabilized by coordination to other neighboring iron octahedra.

Table 2 shows an increase in IS values from samples MF8 to MF6, the sample with the least distorted sites to the sample with the most distorted sites. An increase in IS often is linked to an increase in the average bond length (Hawthorne, 1988; Waychunas *et al.*, 1988). Hence, the increase in IS from sample MF8 to MF6 suggests that Fe–O bond relaxation, that is bond lengthening, occurs at labile sites. Van der Kraan (1973) found interactions of surface ions with neighboring ions weaker, possibly explaining why the present study finds bond relaxation more likely to occur at sites that have fewer neighboring octahedra.

Effect of adsorbed arsenate on the ferrihydrite structure

The Mössbauer spectroscopic results for samples with adsorbed arsenate depended on whether arsenate was adsorbed before or after iron isotopic exchange (Table 2). Sample MF9, for example, that had arsenate adsorbed to ferrihydrite before exchange with ^{57}Fe, had a MQS value of 0.81(2) mm s^{-1}. The MQS value for sample MF9 did not differ significantly from MF5, indicating that the spectra of the unblocked labile sites was essentially unchanged by arsenate adsorption.

The effect of arsenate adsorption after ^{57}Fe surface exchange was investigated with samples MF10a and MF10b. The labile sites of both samples were enriched with ^{57}Fe such that the initial state of the sample was similar to sample MF5; then arsenate was adsorbed for 20 min (sample MF10a) or 72 hr (sample MF10b). The MQS values derived for these two samples suggest that arsenate may have a stabilizing effect on the labile ^{57}Fe sites. Samples MF10a and MF10b showed lower MQS values of 0.79(2) mm s^{-1} and 0.78(2) mm s^{-1}, respectively, relative to sample MF5. If the decrease is truly indicative of reduction in site distortion, arsenate may prevent the iron sites, that were previously more free to develop random local distortions, from distorting to the same extent as in samples MF5 or MF6. Additional time for adsorption did not appear to change significantly the stabilizing effect AsO_4^{-3} had on these Fe sites, as evidenced by the lack of a significant difference between the MQS values for samples MF10a and MF10b.

The ^{59}Fe isotopic exchange results showed that adsorption of arsenate decreased the number of labile iron sites (Figure 4); this observation indicates that the arsenate ions probably blocked at least a portion of the population of labile sites, preventing rapid isotopic exchange. Blocking of the sites might be expected from published studies demonstrating the high activation energy for desorption of arsenate and phosphate (Hingston, 1981). Strong bidentate bonds to adjacent iron octahedra (Waychunas *et al.*, 1993) would prevent the facile exchange of iron isotopes between the solid

and the solution. Mössbauer spectroscopy results indicate that the distortion of the labile sites may be reduced when arsenate is bonded to them by adsorption. The reduced distortion implies that arsenate bonding stabilizes these sites. It seems likely that binuclear, bidentate bonding would impose a stabilizing effect on Fe octahedra with few Fe neighbors by increasing the Fe–M coordination around the octahedra (where M represents either As or Fe). Monodentate complexes also may stabilize the structure of the labile sites, but such an effect would be expected to be smaller than the stabilization caused by bidentate bonding.

CONCLUSIONS

Although ferrihydrite lacks long range structural order, specific sites that indicate differences in reactivity and bonding can be studied. The iron isotopic exchange experiments show that ferrihydrite contains labile and non-labile site populations; the number of sites participating in the faster exchange process was reduced by adsorbing arsenate before the exchange experiment. The labile sites, examined with Mössbauer spectroscopy, are found to have different local environments; sites which exchanged very quickly (within 20 min) had more distorted octahedral geometry relative to sites that were slower to exchange. When bonded to adsorbed arsenate, the distortion of labile sites was slightly reduced. Adsorbed arsenate may decrease the degree of distortion around the octahedra by forming binuclear, bidentate bonds to adjacent Fe octahedra. Using the structure derived from EXAFS (Waychunas *et al.,* 1993), it is reasonable to propose that the labile and non-labile site populations can be assigned to locations within the structure with lesser and greater than average Fe–Fe octahedral coordination, respectively. The sites with lower coordination would presumably be on the ends of dioctahedral chains, whereas sites with greater Fe–Fe coordination would be located in the center of chains and perhaps at locations characterized by a high degree of chain cross-linking.

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REFERENCES

Atkinson, R. J., Posner, A. M., and Quirk, J. P. (1968) Crystal nucleation in Fe(III) solutions and hydroxide gels: *J. Inorganic Nuclear Chem.* **30,** 2371–2381.

Bancroft, G. M. (1973) *Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists:* Halsted Press, New York, 252 pp.

Cardile, C. M. (1988) Tetrahedral Fe^{3+} in ferrihydrite: ^{57}Fe Mössbauer spectroscopic evidence: *Clays & Clay Minerals* **36,** 537–539.

Carlson, L. and Schwertmann, U. (1981) Natural ferrihydrites in surface deposits from Finland and their association with silica: *Geochim. Cosmochim. Acta* **45,** 421–429.

Childs, C. W. and Johnston, J. H. (1980) Mössbauer spectra of protoferrihydrite at 77 K and 295 K, and a reappraisal of the possible presence of akaganeite in New Zealand soils: *Aust. J. Soil Res.* **18,** 245–250.

Combes, J. M., Manceau, A., Calas, G., and Bottero, J. Y. (1989) Formation of ferric oxides from aqueous solutions: A polyhedral approach by X-ray absorption spectroscopy: I. Hydrolysis and formation of ferric gels: *Geochim. Cosmochim. Acta* **53,** 583–594.

Crank, J. (1975) *The Mathematics of Diffusion,* Oxford University Press, Ely House, London, 347 pp.

Eggleton, R. A. and Fitzpatrick, R. W. (1988) New data and a revised structural model for ferrihydrite: *Clays & Clay Minerals* **36,** 111–124.

Fitzpatrick, R. W. (1988) Iron compounds as indicators of pedogenic processes: Examples from the southern hemisphere: in *Iron in Soils and Clay Minerals. NATO ASI Series, Series C: Mathematical and Physical Sciences,* J. W. Stucki, B. A. Goodman, and U. Schwertmann, eds., D. Reidel Publishing Company, Boston, 351–396.

Fuller, C., Davis, J. A., and Waychunas, G. A. (1993) Surface chemistry of ferrihydrite: 2. Kinetics of arsenate adsorption and coprecipitation: *Geochim. Cosmochim. Acta* **57,** 2271–2282.

Fuller, C. and Davis, J. A. (1989) Diel cycles of pH and trace elements in surface waters: Coupling of sorption and photosynthetic processes: *Nature* **340,** 52–54.

Hawthorne, F. C. (1988) Mössbauer spectroscopy: *Spectroscopic Methods in Mineralogy and Geology, Reviews in Mineralogy, Vol. 18,* F. C. Hawthorne, ed., Mineralogical Society of America, Washington, D.C., 255–340.

Hawthorne, F. C. and Waychunas, G. A. (1988) Spectrum fitting methods: *Spectroscopic Methods in Mineralogy and Geology, Reviews in Mineralogy, Vol. 18,* F. C. Hawthorne, ed., Mineralogical Society of America, Washington, D.C., 63–98.

Hingston, F. J. (1981) A review of anion adsorption: *Adsorption of Inorganics at Solid-Liquid Interfaces,* M. A. Anderson and A. J. Rubin, eds., Ann Arbor Science, Ann Arbor, Michigan, 51–90.

Johnston, J. H. and Lewis, D. G. (1983) A detailed study of the transformation of ferrihydrite to hematite in an aqueous medium at 92°C: *Geochim. Cosmochim. Acta* **47,** 1823–1831.

Langmuir, D. and Whittemore, D. O. (1971) Variations in the stability of precipitated ferric oxyhydroxides: *Non-Equilibrium Systems in Natural Water Chemistry, Advances in Chemistry Series 106,* R. F. Gould, ed., American Chemical Society, Washington, D.C., 209–234.

Leckie, J. O., Merrill, D. T., and Chow, W. (1985) Trace element removal from power plant wastestreams by adsorption/coprecipitation with amorphous iron oxyhydroxide: Separation of heavy metals and other trace contaminants: *AIChE Symposium Series #243, Vol. 81,* P. W. Peters and B. M. Kim, eds., 28–42.

Manceau, A., Combes, J.-M., and Calas, G. (1990) New data and a revised structural model for ferrihydrite: Comment: *Clays & Clay Minerals* **38**, 331–334.

Martell, A. E. and Smith, R. M. (1974) *Critical Stability Constants, 1: Amino Acids*, Plenum Press, New York, 469 pp.

Murad, E. (1988) The Mössbauer spectrum of "well"-crystallized ferrihydrite: *J. of Magnetism and Magnetic Mater.* **74**, 153–157.

Murad, E., Bowen, L. H., Long, G. J., and Quin, T. G. (1988) The influence of crystallinity on magnetic ordering in natural ferrihydrites: *Clay Miner.* **23**, 161–173.

Murad, E., and Johnston, J. H. (1987) Iron oxides and oxyhydroxides: in *Mössbauer Spectroscopy Applied to Inorganic Chemistry, Vol. 2*, G. J. Long, ed., Plenum Press, New York, 542–547.

Murad, E. and Schwertmann, U. (1980) The Mössbauer spectrum of ferrihydrite and its relation to those of other iron oxides: *Amer. Mineral.* **65**, 1044–1049.

Papelis, C., K. F. Hayes, and Leckie, J. O. (1988) HYDRAQL: A program for the computation of aqueous batch systems including surface-complexation modeling of ion adsorption at the oxide/solution interface: *Tech. Rept.* **306**, Department of Civil Engineering, Stanford University, 130 pp.

Parfitt, R. L., Atkinson, R. J., and Smart, R. St.C. (1975) The mechanism of phosphate fixation by iron oxides: *SSSA Proc.* **39**, 837–841.

Ruby, S. L. (1973) Why MISFIT when you already have χ^2?: *Mössbauer Effect Methodology, Vol. 8*, I. J. Gruverman, ed., 263–276.

Schultz, M. F., Benjamin, M. M., and Ferguson, J. F. (1987) Adsorption and desorption of metals on ferrihydrite: Reversibility of the reaction and sorption properties of the regenerated solid: *Environ. Sci. Technol.* **21**, p. 863.

Schwertmann, U. and Fischer, W. R. (1973) Natural "amorphous" ferric hydroxide: *Geoderma* **10**, 237–247.

Schwertmann, U. and Taylor, R. M. (1977) Iron Oxides: in *Minerals in Soil Environments*, J. B. Dixon and S. B. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 145–180.

Towe, K. M. and Bradley, W. F. (1967) Mineralogical constitution of colloidal "hydrous ferric oxides": *J. of Coll. and Inter. Sci.* **24**, 384–392.

Van der Kraan, A. M. (1973) Mössbauer effect studies of surface ions of ultrafine α-Fe_2O_3 particles: *Phys. Stat. Sol. A* **18**, 215–226.

Waychunas, G. A., Rea, B. A., Davis, J. A., and Fuller, C. C. (1993) Surface chemistry of ferrihydrite: I. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate: *Geochim. Cosmochim. Acta* **57**, 2251–2269.

Waychunas, G. A., Brown, G. E., Ponader, C. W., and Jackson, W. E. (1988) Evidence from X-ray absorption for network-forming Fe^{2+} in molten alkali silicates: *Nature* **332**, 251–253.

Waychunas, G. A. (1979) Mössbauer, X-ray, optical and chemical study of cation arrangements and defect association in Fm3m solid solutions in the system periclase-wustite-lithium ferrite: Ph.D. dissertation, University of California, Los Angeles, 456 pp.