

## INFLUENCE OF STRUCTURAL AND ADSORBED Si ON THE TRANSFORMATION OF SYNTHETIC FERRIHYDRITE<sup>1</sup>

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**Abstract**—The transformation of ferrihydrite to goethite and/or hematite, as influenced by the presence of co-precipitated Si, was investigated by infrared spectroscopy (IR), X-ray powder diffraction (XRD), and transmission electron microscopy (TEM). Ferrihydrite samples having Si/Fe molar ratios ranging from 0 to 1 were synthesized by reacting  $\text{Fe}_2(\text{SO}_4)_3$  with NaOH to an equilibrium pH of 8.2 in the presence of  $\text{Na}_2\text{SiO}_3$ . The XRD pattern of the Si-free sample contained five distinct but weak peaks, whereas the patterns of ferrihydrite samples containing Si had only two broad bands. With an increase of the Si/Fe molar ratio from 0.10 to 1.0, the 2.54-Å XRD peak shifted to 2.97 Å, and broad IR bands were observed at  $990\text{ cm}^{-1}$  (Si–O stretching region) and  $450\text{ cm}^{-1}$  (silicate bending region). The intensities of both IR bands increased with increasing Si/Fe molar ratio.

Ferrihydrite samples were incubated at room temperature in sodium acetate/acetic acid buffer solutions at pH 3, 5, 7, and 10 and in  $\text{CaCO}_3$  suspension at pH 8.3 for 10 months. Additional samples were incubated at pH 12.5 at 24°, 40°, 60°, and 91°C for 36 hr. Room-temperature incubation of ferrihydrite samples having Si/Fe molar ratios  $\geq 0.1$  at pH 3 for one week resulted in the dissolution of Fe and the precipitation of silica gel. Ferrihydrite samples having Si/Fe molar ratios  $\leq 0.05$  transformed to poorly crystalline goethite during room-temperature incubation at pH 5. The rate of transformation and the degree of crystallinity of the product were inversely related to Si/Fe molar ratio, and, with heat treatment, were also dependent on incubation temperature. Siliceous ferrihydrite samples having Si/Fe molar ratios  $\geq 0.10$  did not transform to phases having greater crystallinity during incubation at either room temperature in buffered solutions at pH  $\geq 7$  for as long as 10 months or at pH 12.5 at 91°C for 36 hr. The XRD peak at 2.97 Å did not shift significantly during incubation procedures, providing evidence that the structure of the high-Si ferrihydrite was not significantly altered.

**Key Words**—Adsorption, Crystal structure, Ferrihydrite, Infrared spectroscopy, Silicon, Synthesis, X-ray powder diffraction.

### INTRODUCTION

Ferrihydrite is a poorly crystalline, thermodynamically unstable Fe oxide under surface conditions, and with time transforms to more-crystalline phases. In soils, ferrihydrite typically contains adsorbed anions, due to its highly reactive surface, which tends to participate in ligand bonding. For example, Schwertmann and Fischer (1973), Childs *et al.* (1982), Campbell and Schwertmann (1984), and Manning *et al.* (1985) noted that ferrihydrite in soil usually coexists with silicate anions, which apparently retard or inhibit the transformation of this mineral to more-crystalline products (Herbillon and Tran Vinh An, 1969; Schwertmann and Thalmann, 1976; Carlson and Schwertmann, 1980). The present study was initiated to investigate the transformation of ferrihydrite coprecipitated with different amounts of Si to goethite and/or hematite.

### MATERIALS AND METHODS

#### *Preparation of ferrihydrite*

Ten ferrihydrite samples having Si/Fe molar ratios ranging from 0 to 1 were synthesized as follows: to a 1000-ml Erlenmeyer flask containing 100 ml of water,

150 ml of  $\text{Na}_2\text{SiO}_3$  (concentration was dependent upon the desired Si/Fe molar ratio) was added simultaneously with 242 ml of 0.714 M  $\text{Fe}_2\text{SO}_4$  while stirring vigorously with a magnetic stirrer. The pH was adjusted to 8.2 with NaOH, and the products were incubated for 4 days and then dialyzed to remove the excess salt. The final concentration of Fe in the samples was adjusted to 4 g/liter with deionized water. The Si concentrations of the ferrihydrite samples having Si/Fe molar ratios  $\leq 0.50$  were determined by a 4-hr, pH 3, 0.2 M ammonium-oxalate extraction (McKeague and Day, 1966) and subsequent analysis of the extract. For ferrihydrite samples having Si/Fe molar ratios  $\geq 0.75$ , a white gelatinous precipitate of silica gel was noticed after the samples were treated with pH 3 ammonium oxalate for 4 hr. Therefore, a successive extraction procedure, using the 2.5-min boiling 0.5 M NaOH (Jackson, 1969) and the pH 3 ammonium-oxalate treatments, was used to determine the total Si contents of these samples. The Fe content of each sample was determined by the pH 3 ammonium-oxalate extraction method. Si and Fe were analyzed by atomic absorption spectrophotometry.

#### *Incubation procedures*

*Na-acetate incubation.* Ferrihydrite samples containing 800 mg of Fe were incubated in 2 M sodium ace-

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tate/acetic acid solutions (400 ml) at pH 3, 5, 7, and 10 for 10 months at room temperature ( $23^{\circ} \pm 1^{\circ}\text{C}$ ) to study the influence of pH on the transformation of ferrihydrite to crystalline Fe oxides. Separate samples were incubated in calcite suspensions to simulate a calcareous soil environment having a pH of  $\sim 8.3$ . The pHs of the suspensions incubated at  $\text{pH} \leq 8.2$  did not change appreciably (i.e., by more than 0.5 pH unit) during the 10 months of incubation; however, for the samples incubated at pH 10, the average pH change was about  $-1.3$  units. Aliquots of the suspensions were withdrawn periodically, washed three times with deionized water, and freeze dried.

**Wet-heat incubation.** Suspensions of ferrihydrite (25 mg) in 100 ml of  $\text{H}_2\text{O}$  were adjusted to pH 12.5 using NaOH and incubated at  $24^{\circ}$ ,  $40^{\circ}$ ,  $60^{\circ}$ , and  $91^{\circ}\text{C}$  for 36 hr in a water bath. After incubation, the samples were washed three times with deionized water and freeze dried.

#### Mineral analyses

Freeze-dried samples of ferrihydrite were randomly oriented on double-sided adhesive tape on glass slides, and X-ray powder diffraction (XRD) patterns were obtained using  $\text{CuK}\alpha$  radiation from a Philips-Norelco diffractometer equipped with a graphite monochromator. For infrared (IR) analyses, KBr pellets were made by homogenizing 300 mg of KBr (ground with a mortar and pestle and dried at  $110^{\circ}\text{C}$  for 24 hr) with 3 mg of the oxide and compressing the mixture at 10,000 psi. The IR spectra were recorded using a double-beam Perkin-Elmer 283 spectrophotometer. For transmission electron microscopic (TEM) analyses, the samples were dispersed in distilled water using a sonic bath, and a drop of the suspension was dried on a carbon-coated copper grid. TEMs and electron diffraction patterns of the samples were obtained using a Zeiss 10C transmission electron microscope operated at 60 keV.

## RESULTS AND DISCUSSION

#### X-ray powder diffraction and infrared analyses of Si-containing ferrihydrite

The Si-free ferrihydrite sample gave an XRD pattern similar to, but containing broader and weaker bands than, the five-line XRD pattern of ferrihydrite reported by Carlson and Schwertmann (1980). In addition, weak goethite peaks were present at 4.18, 2.69, and 2.54 Å. For Si-containing samples, broad two-line XRD patterns were observed, with peaks at 2.54 and 1.50 Å (Vempati and Loeppert, 1986). The 2.54-Å peak shifted to 2.97 Å for ferrihydrite samples having Si/Fe molar ratios  $\geq 0.1$ , but the 1.50-Å peak did not shift. A shift of the 2.54-Å peak was also observed by Carlson and Schwertmann (1980) for natural Si-containing fer-

rihydrites. The broad XRD peaks of ferrihydrite samples synthesized in the presence of Si are an indication of less-ordered crystals and/or smaller particle size than for the Si-free ferrihydrite. Eggleton and Fitzpatrick (1988) observed the probable presence of tetrahedrally coordinated  $\text{Fe}^{3+}$  in ferrihydrite and hypothesized that tetrahedral Si may substitute for the tetrahedral  $\text{Fe}^{3+}$ . Recent photoelectron spectroscopy studies (Vempati *et al.*, 1989) support the possible presence of tetrahedrally-coordinated  $\text{Fe}^{3+}$  in ferrihydrite and of tetrahedrally coordinated structural Si in Si-containing ferrihydrite having Si/Fe molar ratios  $\geq 0.10$ . Therefore, the shift of the 2.54-Å peak for ferrihydrite samples having Si/Fe molar ratios  $\geq 0.1$  may have been due to Si incorporated into the ferrihydrite structure.

IR spectra of selected samples are shown in Figure 1. For the Si-free sample, weak IR bands characteristic of goethite are present at 890, 791, 610, and  $400\text{ cm}^{-1}$ . Also, bands attributable to a binuclear-bridging complex between sulfate and ferrihydrite are present at 1170, 1125, 1050, and  $970\text{ cm}^{-1}$ , in agreement with the peak assignments by Harrison and Berkheiser (1982). The sulfate originated from the ferric sulfate used in the synthesis of the ferrihydrite. In the IR patterns of each of the Si-containing samples, Si-O bending vibrations were present as a broad band at  $450\text{ cm}^{-1}$  (Figure 1). The vibration intensity increased with increasing Si/Fe molar ratio (Figure 2). For samples having Si/Fe molar ratios  $\geq 0.10$ , an additional broad IR band attributed to Si-O stretching vibrations was present at  $990\text{ cm}^{-1}$  (Figure 1). The intensity of this band also increased with increasing Si/Fe molar ratio (Figure 3). No IR bands indicative of sulfate were observed for these high-Si samples.

Previously, Vempati and Loeppert (1985) noted that for samples having Si/Fe molar ratios  $\leq 0.05$ , the  $450\text{-cm}^{-1}$  band almost entirely disappeared on treatment of the sample with phosphate. Therefore, monodentately adsorbed silicate, i.e.,  $\text{Fe-O-Si(OH)}_3$  at the oxide surface, was likely a major contributor to the  $450\text{-cm}^{-1}$  band of these samples. For samples having Si/Fe molar ratios  $\geq 0.1$ , the intensities of the  $450\text{-}$  and  $990\text{-cm}^{-1}$  IR bands decreased on phosphate treatment, indicating that a portion of the Si was accessible for displacement. The 110 XRD peak (2.97 Å), however, did not shift following either phosphate or NaOH treatment, evidence that some of the Si was present as an integral part of the ferrihydrite structure. The Si in these samples was likely present as monodentately adsorbed silicate, short silicate chains (polymerized silica; Figure 4), and structural Si.

The ferrihydrite samples examined in this study can be grouped into three classes based on XRD and IR patterns: (1) Si-free ferrihydrite, (2) low-silica ferrihydrite having Si/Fe molar ratios  $\leq 0.05$ , and (3) high-silica ferrihydrite or siliceous ferrihydrite having Si/Fe molar ratios  $\geq 0.1$  (Figure 1).

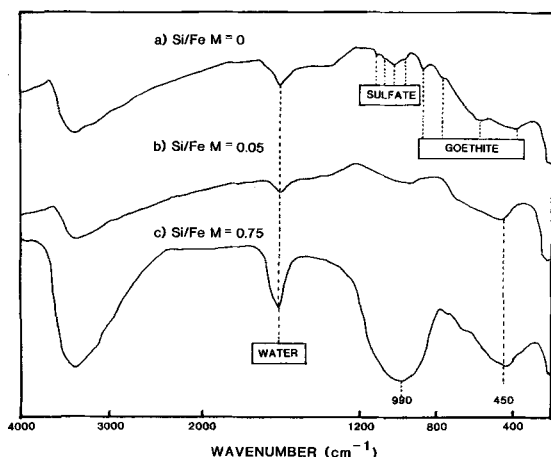


Figure 1. Infrared spectra of ferrihydrite samples: (a) 0 Si, (b) 0.05 Si/Fe molar ratio, and (c) 0.75 Si/Fe molar ratio.

#### Na-acetate incubation

**pH 3.** In the present study, the maximum dissolution of Fe from ferrihydrite was noted at pH 3, irrespective of the Si/Fe molar ratio; however, the transformation of ferrihydrite to goethite was not observed, even after 10 months of incubation and even though the solubility product of goethite was exceeded.

For all ferrihydrite samples having Si/Fe molar ratios  $\geq 0.1$ , silica gel was observed as a transformation product within one week of the initiation of incubation, as indicated by the characteristic IR bands of silica gel at 1077, 963, 797, and 459  $\text{cm}^{-1}$  (Figure 5). In an analogous low pH system, a white gelatinous precipitate of silica gel was noted after ferrihydrite samples having Si/Fe molar ratios of 0.75 and 1.0 had been treated with 0.2 M ammonium oxalate at pH 3 for 4 hr. For ferrihydrite samples having Si/Fe molar ratios  $\geq 0.1$ , the solubility product of silica gel was likely exceeded, resulting in precipitation of this phase. Also, the dissolution of Fe from ferrihydrite at pH 3 probably further enhanced the transformation of siliceous ferrihydrite to silica gel in these samples.

**pH 5.** The IR spectra indicated that ferrihydrite samples having low Si/Fe molar ratios ( $\leq 0.05$ ) transformed to poorly crystalline goethite (Figure 6). For example, after 10 months of incubation of the 0.036 Si/Fe molar ratio sample, the characteristic Fe–OH inner-hydroxyl stretching vibration of goethite at 3130  $\text{cm}^{-1}$  appeared instead as a shoulder at  $\sim 3170 \text{ cm}^{-1}$ . The OH in-plane and out-of-plane IR bending vibrations of goethite appeared as broad bands at 890 and 791  $\text{cm}^{-1}$ , respectively (Figure 6). The broad bands at 400 and 610  $\text{cm}^{-1}$  were likely due to Fe–OH unsymmetrical-stretching and Fe–O symmetrical-stretching vibrations, respectively. The shift of the Fe–O symmetrical-stretching vibration from 630  $\text{cm}^{-1}$  for well-crystalline goethite to 610  $\text{cm}^{-1}$  in this study is an indication of poorer

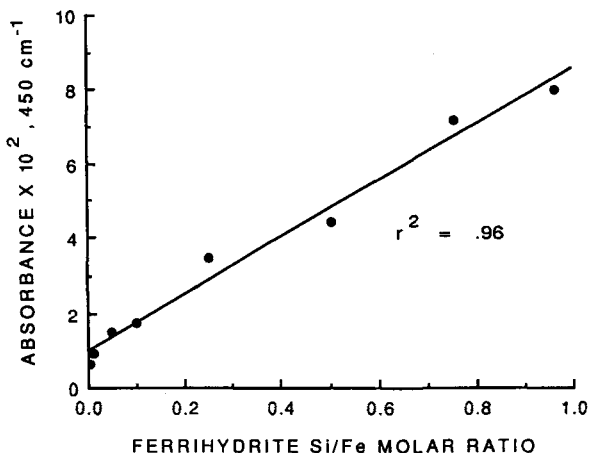


Figure 2. Relationship between peak height of the 450- $\text{cm}^{-1}$  infrared band and ferrihydrite Si/Fe molar ratio.

crystallinity and of minor tilting of the rows of octahedra and weak H-bonding in the unit cell (Cambier, 1986). The amounts of silica dissolved at pH 5 from the ferrihydrite samples having low Si/Fe molar ratios were apparently insufficient to inhibit the transformation to goethite completely; however, the presence of Si influenced the crystallinity of the goethite.

For samples having Si/Fe molar ratios  $\geq 0.75$ , silica gel was identified as a major product after 10 months of incubation; however, goethite was not identified in these samples by TEM, XRD, or IR (Figure 5). Previously, Vempati and Loeppert (1986) observed that the dissolution rates of ferrihydrite samples having Si/Fe molar ratios  $\geq 0.75$  were high compared to rates observed for ferrihydrite samples having lower Si/Fe molar ratios. This more rapid dissolution was attributed to the smaller crystallite sizes and greater reactive surface areas of the former; however, the high Si concentration in solution probably prevented recrystallization as goethite. At the highest Si levels the solutions

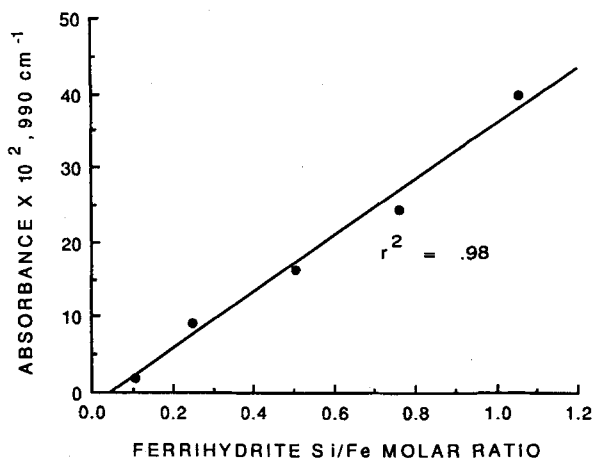


Figure 3. Relationship between peak height of the 990- $\text{cm}^{-1}$  infrared band and ferrihydrite Si/Fe molar ratio.

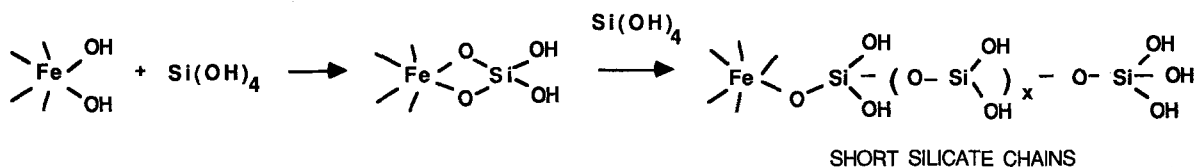


Figure 4. Silicate adsorption model for the  $990\text{-cm}^{-1}$  infrared absorption region.

became supersaturated with respect to silica gel, resulting in the precipitation of this phase.

*pHs 7, 8.2, and 10.* No mineralogical transformations were observed for ferrihydrite samples incubated at pHs 7, 8.2, or 10. The concentration of total dissolved Fe was at a minimum in the pH range of 6–10 (Figure 7). Moreover, the rate of dissolution of the Fe oxide was likely at a minimum in this pH range; therefore, a slow rate of transformation of ferrihydrite to more crystalline Fe oxides would be expected. The absence of IR bands characteristic of silica gel, even after 10 months of incubation, suggests that the Si remained in intimate association with the Fe oxide. The release of Si into solution and subsequent precipitation of silica gel probably required the dissolution of the Fe-oxide matrix, as was observed at pH 3 for ferrihydrite samples having Si/Fe molar ratios  $\geq 0.1$ . The relatively small amounts of Si that were released at pH 7–10 were probably readily re-adsorbed at the oxide surface.

Following incubation of the 0.036 Si/Fe molar ratio ferrihydrite sample for 10 months at pH 8.3 or 10, the sulfate anions were desorbed, and a broad IR band attributable to silicate was observed at  $986\text{ cm}^{-1}$  (Figure 8). The displacement of sulfate at pHs 8.3 and 10 was likely due to the replacement of specifically bound sulfate by silicate at pHs greater than the point of zero charge (pzc) (Motts, 1978). Because the samples were incubated in glass, some Si was probably released from the glass and subsequently contributed to the  $986\text{-cm}^{-1}$  IR band. Hingston *et al.* (1972) reported maximum

sulfate adsorption at pH 4 and maximum silicate adsorption at pH 10. Similarly, in the present study, sulfate adsorption was observed at the lower pH; whereas, at the higher pH, silicate anions replaced sulfate from ligand exchange sites.

For samples incubated at pH 10, an additional IR band was observed at  $1397\text{ cm}^{-1}$ , which was most likely due to the symmetrical-stretching vibration of the carboxylate group of ligand-bound acetate (Figure 8).

#### Wet-heat incubation study

On incubation of ferrihydrite at pH 12.5 for 36 hr, the temperature required for transformation to goethite and/or hematite was dependent on the Si/Fe molar ratio (Table 1). Samples having Si/Fe molar ratios  $\leq 0.05$  transformed to goethite and hematite on treatment at  $91^\circ\text{C}$ .

Goethite and hematite formed during the incubation of the Si-free ferrihydrite were relatively well crystalline; e.g., the half-height peak widths of the principal XRD peaks of goethite were about  $0.25^\circ 2\theta$ . The goethite crystals were predominantly acicular, but some multidomainic crystals were also observed; hematite particles were electron dense and globular (Figure 9). For goethite formed from the Si-free ferrihydrite, IR bands were observed at  $3130\text{ cm}^{-1}$  for inner-OH vibrations and at  $890$  and  $794\text{ cm}^{-1}$  for in-plane and out-of-plane OH-bending vibrations, respectively (Figure 10a). The Fe–O symmetrical stretching and Fe–OH unsymmetrical stretching bands for goethite at  $640$  and

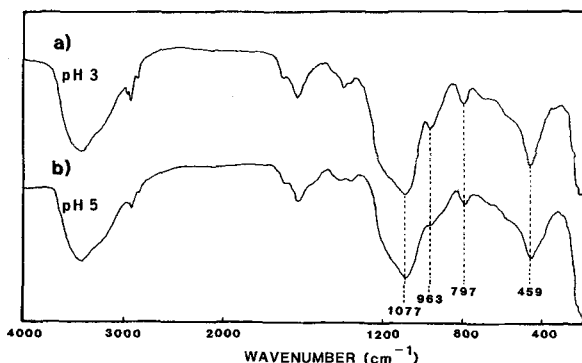


Figure 5. Infrared spectra of siliceous ferrihydrites: (a) 0.25 Si/Fe molar ratio and incubated at pH 3 for one week; and (b) 0.75 Si/Fe molar ratio and incubated at pH 5 for 10 months.

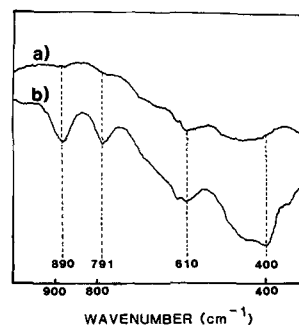


Figure 6. Infrared spectra of a poorly crystalline goethite formed during the incubation of the 0.036 Si/Fe molar ratio ferrihydrite sample in Na acetate at pH 5 for (a) 1 week and (b) 10 months.

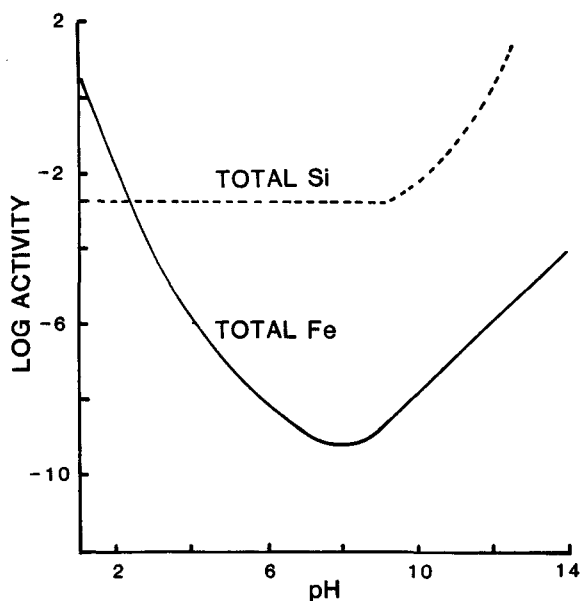


Figure 7. Influence of pH on concentrations of total dissolved Fe and Si in equilibrium with noncrystalline Fe oxide and noncrystalline silicate, respectively (thermodynamic constants from Lindsay, 1979).

400  $\text{cm}^{-1}$ , respectively, were also observed. The lattice vibrations for hematite, which has a  $D_{3d}^5$  space group, were present at 630 (shoulder), 550, 450, 397, and 335  $\text{cm}^{-1}$ .

For ferrihydrite samples having Si/Fe molar ratios  $>0$  but  $\leq 0.05$ , the intensities of the 890- and 797- $\text{cm}^{-1}$  bands decreased as the silicate content of the ferrihydrite increased (Figure 11), indicating that the amount and, possibly, the crystallinity of the goethite decreased with increasing silicate content of the ferrihydrite. Inasmuch as goethite is formed by the dissolution of ferrihydrite (Feitknecht and Michaelis, 1962), the silicate species in solution may have retarded crystal growth, resulting in smaller crystals, and/or influenced the degree of crystallinity of the goethite. The IR bands of hematite were also affected by the silicate content

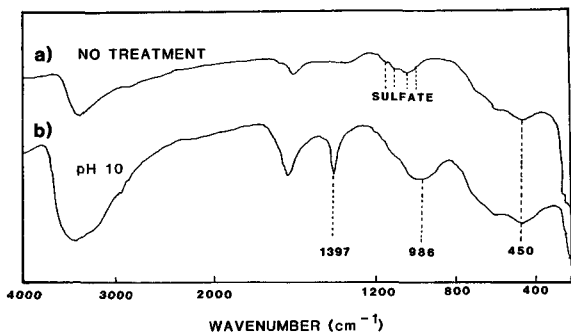


Figure 8. Infrared spectra of the 0.036 Si/Fe molar ratio ferrihydrite sample: (a) untreated, and (b) following incubation at pH 10 for 10 months.

Table 1. Temperature at which Si-containing ferrihydrite samples transformed to goethite and hematite during the pH 12.5 and 36-hr incubations.

Sample Si/Fe molar ratio	Transformation temperature ( $^{\circ}\text{C}$ )
0.0	40
0.001	60
0.01	60 <sup>1</sup>
0.05	91

<sup>1</sup> Goethite and hematite X-ray powder diffraction peaks were less intense in this sample compared with the ferrihydrite having 0.001 Si/Fe ratio.

of the ferrihydrite; i.e., the bands at 550, 450, and 335  $\text{cm}^{-1}$  became less intense and broader as the silicate content of the ferrihydrite increased (Figure 11). Also, no IR absorption bands were observed in the region of 397  $\text{cm}^{-1}$  for hematite formed from the Si-containing ferrihydrite samples, as was observed for hematite formed from the Si-free ferrihydrite. This difference in the IR vibrations of hematite formed from silicate-free vs. silicate-containing ferrihydrite may have been due to differences in particle morphology and particle size of the hematite product (Rendon and Serna, 1981).

For the incubation products of the Si-containing ferrihydrite samples having Si/Fe molar ratios  $\leq 0.01$ , a strong silicate adsorption band at 1003  $\text{cm}^{-1}$  and a weak band at 1150  $\text{cm}^{-1}$  (with shoulders at 950 and 1080  $\text{cm}^{-1}$ ) were noted (Figure 11a). These vibrations suggest the reduced symmetry of the silicate anion, perhaps the  $C_{2v}$  symmetry, as has been observed for binuclear-bridging complexes of phosphate or sulfate to goethite (Parfitt *et al.*, 1975) and ferrihydrite (Harrison and Berkheiser, 1982). For the sample having a Si/Fe molar ratio of 0.05, only a weak band was observed at 999  $\text{cm}^{-1}$  (Figure 11b), possibly due to polymerized Si. The differences in the 1000- $\text{cm}^{-1}$  IR re-

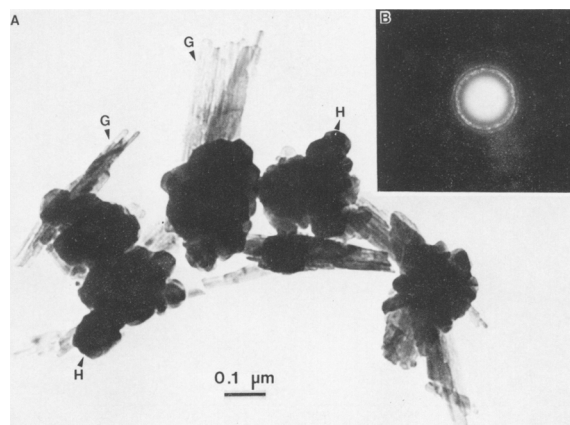


Figure 9. Transmission electron micrographs (A) and electron diffraction patterns (B) of goethite and hematite formed during the incubation of Si ferrihydrite at pH 12.5 and 91 $^{\circ}\text{C}$  for 36 hr.

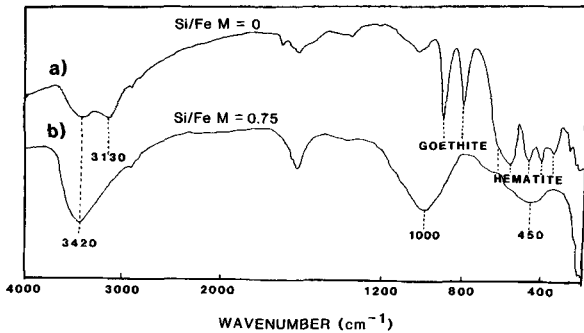


Figure 10. Infrared spectra of ferrihydrite samples after incubation at pH 12.5 and 91°C for 36 hr.

gion between the 0.001 and 0.05 Si/Fe molar ratio samples reflected differences in the predominant silicate forms, most likely ligand-bound silicate anions in the former and polymerized silica, i.e.,  $-O-Si-O-Si-$  bonds in the latter.

Ferrihydrite samples having Si/Fe molar ratios  $\geq 0.1$  did not transform to goethite and/or hematite during pH 12.5 incubations (Figure 10). Incubation resulted in reduction in intensity of both the 450- and 990- $cm^{-1}$  IR bands, indicating that monodentately adsorbed Si and/or silicate chains may have been partly desorbed or altered during the incubation process; however, the 2.97-Å XRD peak did not shift significantly, suggesting that the structure of the high-Si ferrihydrite was not significantly altered. The results of the wet-heat incubation study indicate that structural Si prevented the topotactic transformation of ferrihydrite to hematite. Also, high Si concentrations in solution prevented the nucleation and subsequent crystal growth of goethite from solution.

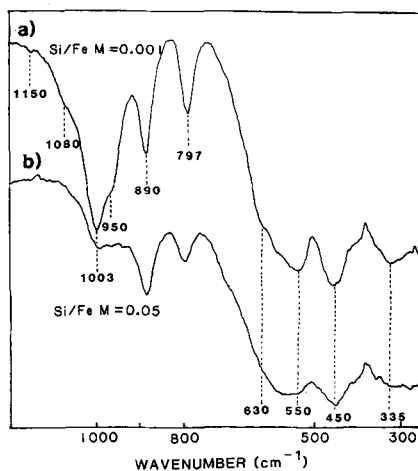


Figure 11. Infrared spectra of ferrihydrite samples having Si/Fe molar ratios  $\leq 0.05$  after incubation at pH 12.5 and 91°C for 36 hr: (a) 0.001 Si/Fe molar ratio; and (b) 0.05 Si/Fe molar ratio.

## SUMMARY

The coexistence of silicate with ferrihydrite affected the transformation of this poorly crystalline Fe oxide to goethite and/or hematite. In natural systems the rate of transformation of ferrihydrite containing adsorbed and/or coprecipitated silicate is probably influenced by Si content, mechanism of silicate bonding, pH, and temperature. Siliceous ferrihydrite (Si/Fe molar ratios  $\geq 0.10$ ), formed during the coprecipitation of Fe oxide with silicate, would probably be stable for extended periods of time at pH  $\geq 7$ , even at elevated temperature.

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