INFLUENCE OF CITRATE ON THE KINETICS OF Fe(II) OXIDATION AND THE FORMATION OF IRON OXYHYDROXIDES[1]

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Abstract—The rate of Fe(II) oxidation at a constant rate of oxygen supply in the presence of citrate was measured at pH 6.0 at various citrate/Fe(II) molar ratios at 23.5°C in 0.01 M ferrous perchlorate system. The kinetics followed a first-order reaction with respect to Fe(II) concentration at constant pH (6.0) and aeration (5 ml/min). The rate constant decreased exponentially from 41.3×10^{-4} to 7.6×10^{-4}/min with an increase in the citrate/Fe(II) molar ratio from 0 to 0.1.

The nature of the hydrolytic products formed after 120 min of oxidation was arrived at by X-ray powder diffraction (XRD), infrared spectrometry (IR), and transmission electron microscopic (TEM) analyses. In the absence of citrate, goethite (α-FeOOH) and poorly crystalline lepidocrocite (γ-FeOOH) were the oxidation products formed at pH 6.0. The formation of lepidocrocite was promoted at the expense of goethite at citrate/Fe(II) molar ratios of 0.0005 to 0.005. The formation of lepidocrocite was especially pronounced at a citrate/Fe(II) molar ratio of 0.001, as observed from the width at half height (WHH) and the area of the 020 XRD peak of lepidocrocite. At a citrate/Fe(II) molar ratio of 0.01, however, the crystallization was perturbed resulting in the formation of noncrystalline Fe oxides, and no precipitate was observed at a citrate/Fe molar ratio of 0.1. The strong complexation of Fe(II) with citrate retarded the kinetics of Fe(II) oxidation and the formation and hydrolysis of Fe(III). The complexation, electrostatic, and steric effects of the coexisting citrate anions in solution apparently influenced the oxygen coordination and the way by which the double rows of edge-sharing $Fe(O,OH)_6$ octahedra linked during crystallization, resulting in the formation of lepidocrocite.

Key Words—Citrate, Goethite, Hydrolysis, Iron oxyhydroxide, Lepidocrocite, Oxidation.

INTRODUCTION

The effect of pedogenetic environments on the transformation of ferrihydrite that formed from hydrolysis and aging of Fe(III) solutions has been extensively investigated (see, e.g., Cornell, 1987; Schwertmann and Taylor, 1989). In an aqueous weathering environment, the oxidation products of Fe(II) solutions are important, because Fe is commonly mobilized as Fe(II) during weathering under the Eh-pH regime of natural soil environments. The rate of Fe(II) oxidation at a constant rate of oxygen supply can be influenced by pH, temperature, and the presence of ions, such as Mn^{2+}, Cu^{2+}, Co^{2+}, and $H_2PO_4^-$ (Stumm and Lee, 1961), and, thus, it should influence the nature of the hydrolytic products in an oxidizing Fe(II) system. Fe(II) is capable of forming complexes with organic matter, and such ligand stabilization has been suggested as an explanation for the apparent presence of Fe(II) in oxic solutions that contain relatively high levels of organic matter (Morgan and Stumm, 1964). The rate of oxidation of Fe(II) in natural waters was found by Sung and Morgan (1980) and Davison and Seed (1983) to

follow first-order kinetics with respect to Fe(II) concentration. Stumm and Lee (1961) and Theis and Singer (1973) demonstrated that the organic ligands decrease the rate constant of Fe(II) oxidation. The differences in the degree of the rate constant of Fe(II) oxidation in the presence of complexing ligands has been attributed to the relative stability of the Fe(II)-ligand complex (Krishnamurti and Huang, 1990a).

The kinetics of Fe(II) oxidation should control the formation and hydrolysis of Fe(III) and modify the crystallization processes of the resultant hydrolytic products of Fe(III). The influence of a few organic ligands on the precipitation products of Fe(II) has also been studied (Schwertmann *et al.*, 1984; Taylor *et al.*, 1987); however, the relationship between the effect of organic ligands on the kinetics of Fe(II) oxidation and the resultant hydrolytic products of Fe(III) remains obscure. The influence of complexing ligands, at different ligand/Fe molar ratios, on the kinetics of Fe(II) oxidation and the resultant formation of the hydrolytic products of Fe(III) should therefore be investigated. The objective of the present study was to examine the influence of citrate, one of the most common organic ligands in natural soil environments, on the kinetics of Fe(II) oxidation and the resultant hydrolytic products of Fe(III) at a series of citrate/Fe molar ratios ranging from 0 to 0.1.
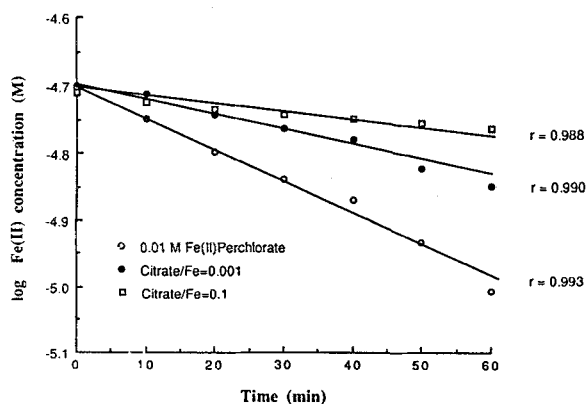

28

Figure 1. Time function of Fe(II) concentration in 0.01 M ferrous perchlorate system as influenced by citrate at pH 6.00 and 23.5°C.

MATERIALS AND METHODS

A 0.01 M ferrous perchlorate solution was made by dissolving 362.8 mg of $Fe(ClO_4)_2 \cdot 6H_2O$ (Pflatz & Bauer Inc., Waterbury, Connecticut) in 100 ml of deionized-distilled water, in which N_2 was constantly bubbled, and adding suitable amounts of citric acid ($C_6H_8O_7 \cdot H_2O$, BDH, Analar grade) to produce citrate/Fe molar ratios of 0.0003, 0.0005, 0.001, 0.005, 0.006, 0.008, 0.01, and 0.1. The citrate/Fe molar ratio refers to the initial citrate/Fe(II) molar ratio of the solution in the system. The pH of the solution was adjusted to 6.00 with 0.1 M NaOH at a constant temperature of 23.5°C using a Metrohm titroprocessor (Model 672) in a set-mode. When the pH of the solution was stabilized at 6.00, the N_2 bubbling was replaced by air (5 ml/min), controlled by a regulator (no attempt was made to remove CO_2 from the air). A constant stream of N_2, however, was allowed to flow above the surface of the solution to prevent oxidation of Fe(II) by atmospheric oxygen. The pH of the solution was maintained at 6.00 ± 0.05 with 0.1 M NaOH. Aliquots of 1 ml of the solution were removed at different times and added to 1 ml of 6 M HCl to quench further oxidation of Fe(II) (Tamura et al., 1976). The Fe(II) concentration in the aliquots was determined spectrophotometrically with 2,4,6-tri(2'-pyridyl)-1,3,5-triazine (TPTZ), using fluoride as a masking agent for Fe(III) (Krishnamurti and Huang, 1990b). A 1-ml sample aliquot was added to 1 ml of 6 M HCl and diluted to about 15 ml; 2 ml of 2 M ammonium fluoride, 2 ml of 0.075% TPTZ, and 4 ml of ammonium acetate-acetic acid buffer (pH 4.5) were added in that order, swirling the solution after the addition of each reagent. The solution was diluted to 25 ml with deionized distilled water, and the absorbance was measured at 595 nm on a Pye-Unicam SP6-500 UV spectrophotometer. The molar absorptivity at 595 nm was determined to be 2.15×10^4 liter/M·cm with an accuracy of >1%.
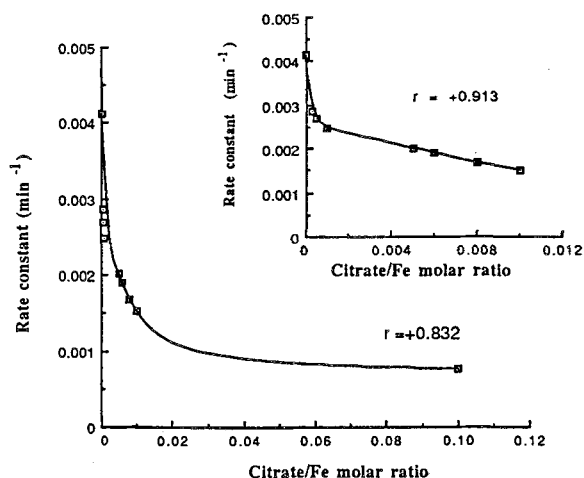
The oxygenation was terminated after 120 min, and

Figure 2. Relationship between rate constant of Fe(II) oxygenation and citrate/Fe molar ratio.

the hydrolytic product of Fe(III) formed through oxidation of Fe(II) at a series of citrate/Fe molar ratios was recovered by ultrafiltration (0.01-μm nitrocellulose filter) in an N_2 atmosphere. The hydrolytic product was examined by X-ray powder diffraction (XRD) on a Philips (Model PW 1031) X-ray diffractometer using Mn-filtered FeKα radiation at 35 kV and 16 mA, by infrared spectrometry (IR) on a Perkin Elmer infrared spectrophotometer (Model 983) using the KBr pellet technique (1 mg of sample mixed with 200 mg of KBr), and by transmission electron microscopy (TEM) using a Philips EM400 transmission electron microscope at 60 kV.

RESULTS

Kinetics of Fe(II) oxidation

The kinetics of oxidation of Fe(II) in aqueous solutions has been studied extensively (e.g., Davison and

Table 1. Rate constants of Fe(II) oxidation and nature of Fe oxides formed in absence and presence of citrate in ferrous perchlorate-NaOH system at pH 6.00 and 23.5°C.

Initial citrate/Fe molar ratio	Rate constant $(min^{-1}) \times 10^4$	XRD[1]		
			020 peak of lepidocrocite	
		Dominant Fe-minerals	WHH ±0.02 (°2θ)	Area (mm²)
0	41.3 ± 2.0	G, L	1.40	40 ± 5
0.0003	28.6 ± 3.5	L, G	1.00	97 ± 5
0.0005	26.9 ± 1.8	L	1.00	124 ± 12
0.0010	24.4 ± 3.0	L	0.80	263 ± 3
0.0050	20.2 ± 1.8	L	1.10	82 ± 4
0.0060	19.1 ± 1.5	L	1.20	25 ± 3
0.0080	16.8 ± 0.6	L	1.20	10 ± 3
0.0100	15.2 ± 0.7	PC	n.a.[2]	n.a.
0.1000	7.6 ± 0.7	no ppt	n.a.	n.a.

[1] X-ray powder diffraction data. WHH = width at half height; L = lepidocrocite; G = goethite, PC = poorly crystalline.
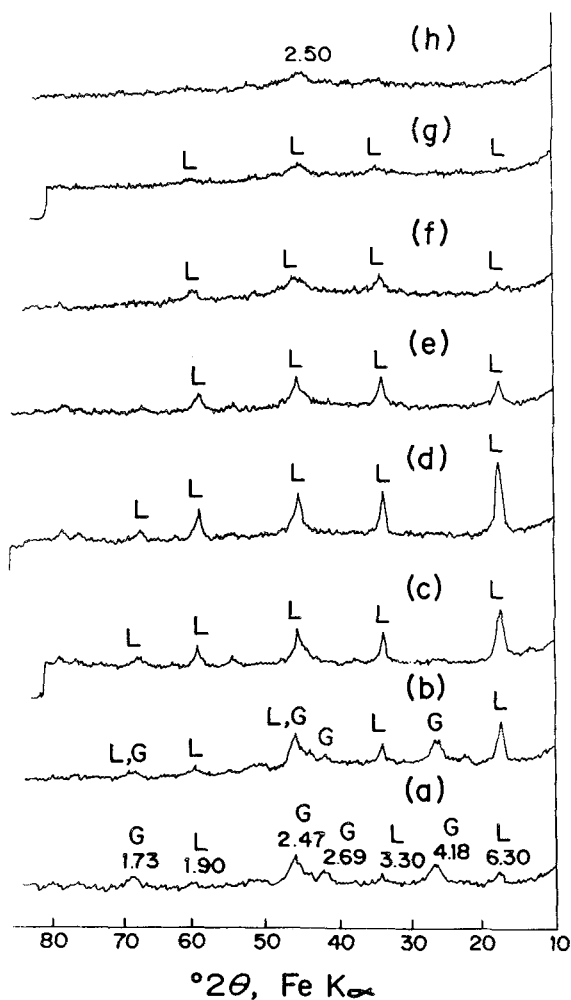[2] n.a. = not applicable.

Figure 3.   X-ray powder diffractograms of hydrolytic products of iron formed in 0.01 M ferrous perchlorate-NaOH system at pH 6.0 (a) in absence of citric acid, and in presence of citric acid at citrate/Fe molar ratios of (b) 0.0003, (c) 0.0005, (d) 0.001, (e) 0.005, (f) 0.006, (g) 0.008, and (h) 0.01. d-values are in Å. L = lepidocrocite, G = goethite.
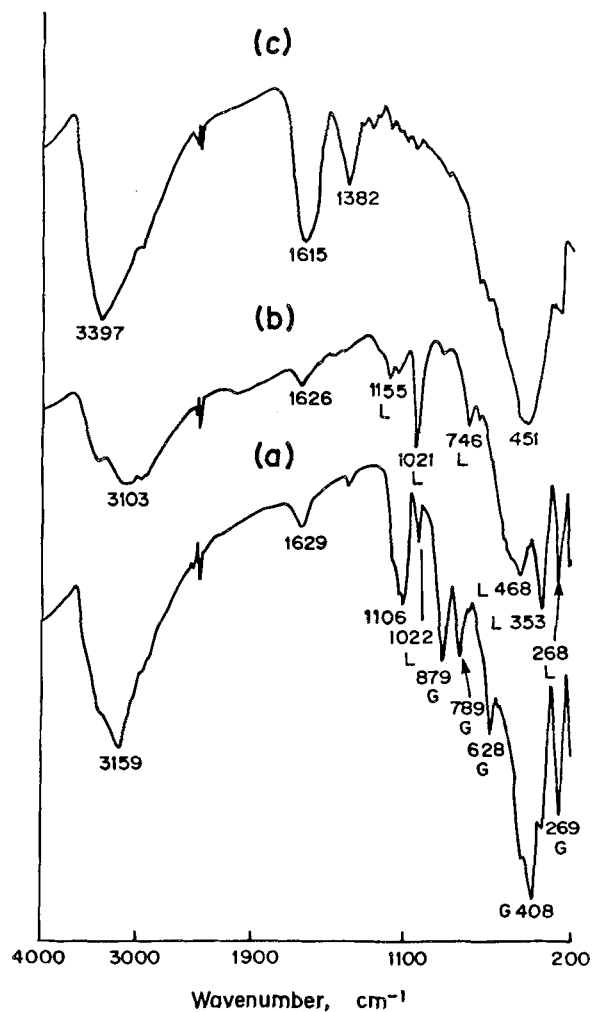

Figure 4.   Infrared spectra of hydrolytic products of iron formed in the 0.01 M ferrous perchlorate-NaOH system at pH 6.0 (a) in absence of citric acid, and in presence of citric acid at citrate/Fe molar ratios of (b) 0.001 and (c) 0.01.

Seed, 1983), and the rate equation has been reported as

$$-d(Fe^{2+})/dt = k(Fe^{2+})(O_2)(OH^-)^2. \qquad (1)$$

At constant pH and pO_2, Eq. (1) reduces to a first-order equation, which integrates to:

$$[Fe(II)] = [Fe(II)]_0 exp(-k't), \qquad (2)$$

where $[Fe(II)]_0$ and $[Fe(II)]$ are the Fe(II) concentrations at a time interval of 0 and t min, respectively, and k' is the rate constant of Fe(II) oxidation at constant pH and pO_2.

Figure 1 shows the time function of the concentration of Fe(II) during the oxidation of 0.01 M ferrous perchlorate in the presence of citrate at different citrate/Fe molar ratios. The rate constant of Fe(II) oxidation

decreased exponentially from 41.3×10^{-4} to 7.6×10^{-4}/min with an increase in the citrate/Fe(II) molar ratio from 0 to 0.1 (Figure 2; Table 1). At the high concentration of 0.001 M citrate (citrate/Fe(II) molar ratio of 0.1), the proportion of Fe(II) bound as Fe(II)-citrate complex was dominant, thereby stabilizing Fe(II) in solution, and no precipitate was observed even after 120 min of oxygenation.

Nature of hydrolytic products of oxidation

In the absence of citrate, the hydrolytic product formed at pH 6.0 was dominantly goethite (α-FeOOH), with small amounts of lepidocrocite (γ-FeOOH). The XRD pattern (Figure 3a) had the characteristic peaks of goethite at 4.18, 2.69, 2.47, and 1.73 Å and those of lepidocrocite at 6.30, 3.30, and 1.90 Å. The IR spectra of the product (Figure 4a) had the characteristic absorption bands of goethite at 879, 789, 628, 408,
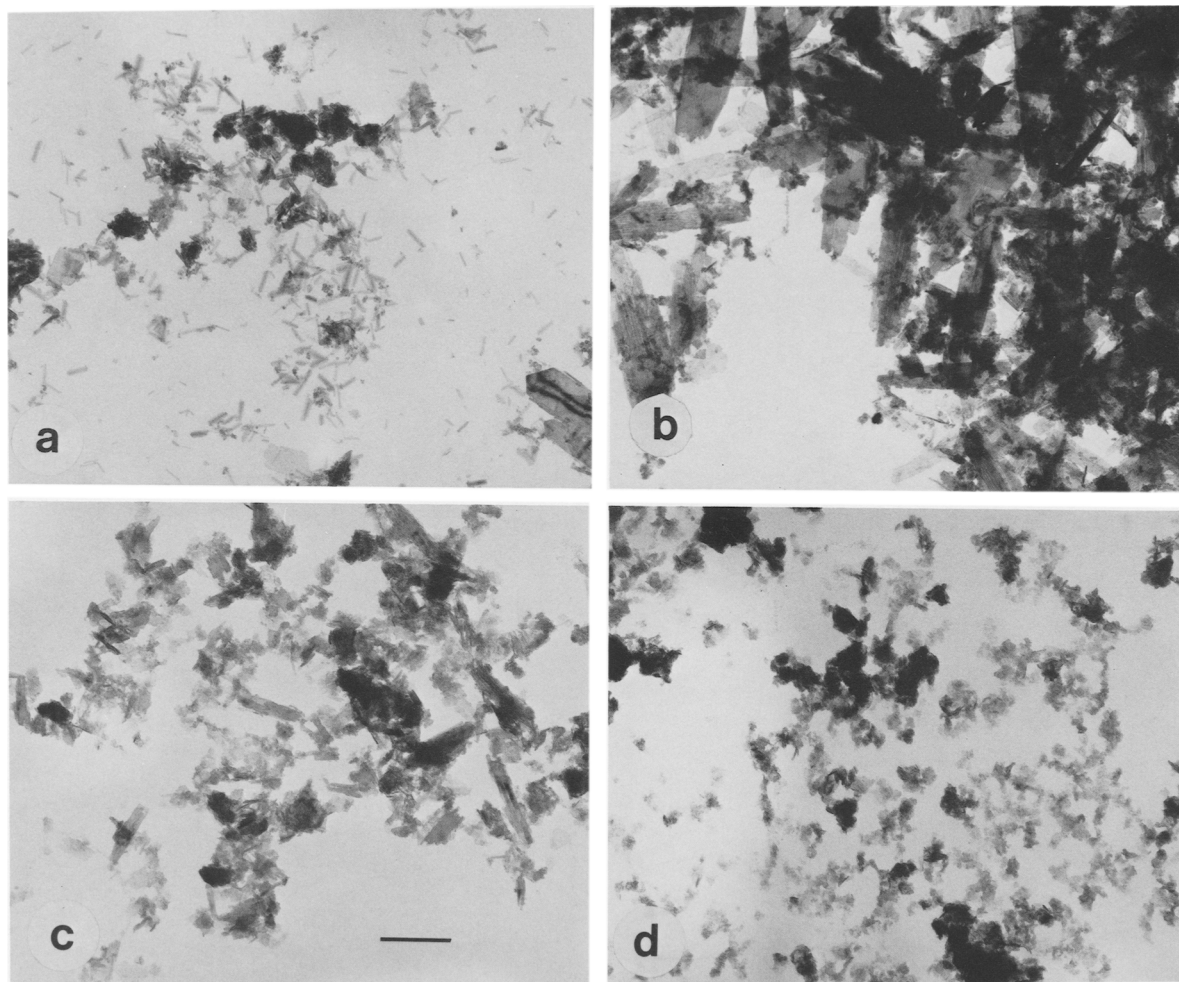
Figure 5. Transmission electron micrographs of hydrolytic products of iron formed in 0.01 M ferrous perchlorate-NaOH system at pH 6.0 (a) in absence of citric acid, and in presence of citric acid at citrate/Fe molar ratios of (b) 0.001, (c) 0.005, and (d) 0.01. Scale bar = 0.1 μm for all micrographs.

and 269 cm^{-1} and that of lepidocrocite at 1022 cm^{-1}. The other characteristic bands at 1155, 746, 468, and 353 cm^{-1} of lepidocrocite are not distinct in Figure 4a due to the small amounts of poorly crystalline lepidocrocite present. The bands at 879 and 789 cm^{-1} of goethite and 1022 cm^{-1} of lepidocrocite are attributed to OH-deformation frequencies (see Russell, 1987). The bands at 628 and 408 cm^{-1} are attributed to the Fe–O stretching frequencies (Farmer, 1975). The band at 1106 cm^{-1} (Figure 4a) is attributed to the ClO$_4^-$ ligand (Socrates, 1980). The TEMs of the product (Figure 5a) show numerous acicular needles and a few laths, characteristic of goethite and lepidocrocite, respectively (Nadeau and Tait, 1987).

The strong complexation of citrate with Fe(III) controlled the hydrolysis of Fe(III) and the crystallization of the hydrolytic product. The formation of goethite was inhibited at the citrate/Fe molar ratios >0.0005 (Figure 3c), as evident by the absence of the charac-

teristic XRD peak (4.18 Å, Figure 3c) and the characteristic OH-deformation frequencies at 879 and 789 cm^{-1} in the IR spectra (Figures 4b and 4c) of goethite. The formation of lepidocrocite was promoted steadily by increasing the citrate/Fe molar ratio from 0 to 0.001. This is evident from the width at half height (WHH) and the area of the 020 characteristic peak (at about 6.30 Å) of lepidocrocite (Figures 3a–3d, Table 1) and the sharp characteristic OH-deformation bands at 1155, 1021, and 746 cm^{-1} in the IR spectra of the product (Figure 4b). A weak band at about 880 cm^{-1} was probably due to traces of goethite not identified in the XRD pattern. The TEMs of the product show well-developed laths (Figure 5b) characteristic of lepidocrocite (Nadeau and Tait, 1987). Increased levels of citrate suppressed the formation of lepidocrocite, as can be seen from the decrease in the size of the laths of lepidocrocite formed (Figure 5c) and from the increase in the WHH and decrease in the area of the 020 peak of

lepidocrocite (Table 1). The broadening of the XRD peaks is attributed to the decrease in crystallinity and/or particle size.

The crystallization process was inhibited at a citrate/Fe molar ratio of 0.01, resulting in the formation of noncrystalline Fe oxides that are characterized by a weak, broad XRD peak at 2.50 Å (Figure 3h) and by IR absorption bands at 1382 and 451 cm^{-1} (Figure 4c). The band at 1382 cm^{-1} can be attributed to the COO-bending vibration of the citrate complexed with Fe(III) (Schnitzer, 1978), and the band at 451 cm^{-1} can be attributed to the Fe–O octahedral vibrations (Farmer, 1975) in the Fe oxides formed. The absence of 1720 cm^{-1} (C = O of COOH) and 1200 cm^{-1} (C–O stretch of OH-deformation of COOH) bands also indicate the presence of COO$^-$ groups, which likely complexed with Fe oxides. The TEMs of the product formed at a citrate/Fe molar ratio of 0.01 show aggregates of irregularly shaped particles (Figure 5d). The IR absorption bands observed at 3103, 3159, and 3397 cm^{-1} and at 1615–1629 cm^{-1} (Figure 4) can be attributed to the hydrogen-bonded OH-stretching frequencies in the Fe oxides formed and the OH-bending frequencies of the adsorbed water (Ryskin, 1974). No precipitate was observed at a citrate/Fe molar ratio of 0.1.

DISCUSSION

In slightly acidic solutions, Fe(II) exists in solution mainly as Fe^{2+} ions (Baes and Mesmer, 1976). In the absence of citrate, and in the presence of poorly complexing perchlorate ligand, the oxidation of Fe(II) and its subsequent hydrolysis can be visualized as:

$$Fe^{2+} \rightarrow Fe^{3+} \rightarrow Fe(OH)^{2+} \rightarrow Fe(OH)_2{}^+.$$
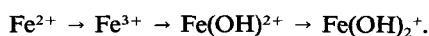
The ferric hydroxo-complex should polymerize with an increase in the concentration of Fe(OH)$_2{}^+$ (Misawa *et al.*, 1974). The hydrolysis-precipitation process of Fe(III) proceeds by progressive elimination of H$^+$, followed by formation of polymeric species with ol- and oxo-linkages (Rollinson, 1956; Stumm and Morgan, 1962; Dousma and DeBruyn, 1976). These polycations form over a wide range of OH/Fe ratios and age into an easily recognizable goethite (α-FeOOH) precipitate (Murphy *et al.*, 1976a, 1976b, 1976c). The relationship between the spherical polycations of Murphy *et al.* (1976a, 1976b, 1976c) and ferrihydrite that forms by the hydrolysis of Fe(III) solutions (Towe and Bradley, 1967; Chukhrov *et al.*, 1973) is not clearly understood. Even though the size and shape appear to be similar, Murphy *et al.* (1976a, 1976b, 1976c) obtained no indication of structure in the polycations. Moreover, the pathway of conversion of ferrihydrite to goethite is thought to occur by dissolution and precipitation (Fischer and Schwertmann, 1975).

Theis and Singer (1973) reported that citrate had no effect on the rate of Fe(II) oxidation even though initially for 10 min it accelerated the oxidation. On the other hand, the data obtained in the present study showed that the citrate that formed a stable complex with Fe(II) (log K = 4.40, Sposito and Mattigod, 1979) retarded the oxidation of Fe(II) considerably (Figures 1 and 2; Table 1). This is in agreement with the theoretical conclusions of Pankow and Morgan (1981). Increasing levels of citrate stabilized Fe(II) (i.e., retardation of oxidation) by attenuating [Fe^{2+}], because increasing levels of citrate increased the proportion of Fe^{2+} bound as Fe(II)-citrate complex, which therefore decreased the proportion of Fe(II) present as Fe^{2+}. The oxidative consumption rate at constant pH and constant rate of oxygen supply, viz., k(Fe^{2+})(OH$^-$)^2(O$_2$), hence, decreased, resulting in a decrease in amount of Fe(III) formed.

The decrease in the rate of Fe(II) oxidation should have favored the thermodynamically more stable goethite over lepidocrocite (Schwertmann, 1959); however, in the presence of citrate, the formation of lepidocrocite was promoted at the expense of goethite. The oxidation of Fe(II) and the subsequent hydrolysis of Fe(III) were strongly influenced by the Fe(II)- and Fe(III)-citrate complexation. The Fe(II)-citrate complexation retarded the kinetics of Fe(II) oxidation, which controlled the kinetics of formation of Fe(III). The strong complexation of Fe(III) with citrate apparently influenced the kinetics of Fe(III) hydrolysis and substantially modified the crystallization processes of the hydrolytic products of Fe. The complexation and electrostatic and steric effects of the coexisting citrate anions, which have stronger affinities to Fe(III) (log K = 10.69, Sposito and Mattigod, 1979) than perchlorate ion (log K = 0.30, Hogfeldt, 1982) apparently influenced the oxygen coordination in the resulting precipitate.

Even though both goethite and lepidocrocite crystallize in the orthorhombic system, the coordination of O atoms is different (Murray, 1979). In goethite, each oxygen is linked to three Fe atoms in octahedral positions and a hydrogen, which is strongly localized to a particular oxygen; in lepidocrocite, however, two kinds of oxygen atoms are present, one linked to four Fe atoms in octahedra, and the other bonded to two Fe atoms and two OH ions, one of which corresponds to a hydrogen bond, O–H. . .O. The hydrogen atom occupies a central position between two oxygen atoms, i.e., the layers consisting of oxo-bridges are held together by hydrogen bonds. Further, both lepidocrocite and goethite consist of double rows of edge-sharing [Fe(O,OH)$_6$] octahedra, but they differ in the way that these double rows are linked together (Murray, 1979). The coexisting citrate anions possibly exert a significant effect on the oxygen coordination and play a positive role in the way in which the double rows are linked during crystallization, resulting in the formation of lepidocrocite. At the optimum concentration of citrate (citrate/Fe molar ratio of 0.001), the oxygen coordi-

nation and the way the edge-sharing [Fe(O,OH)$_6$] octahedra were linked together during the crystallization apparently resulted in highly ordered and crystalline lepidocrite. At higher concentrations of citrate (citrate/Fe molar ratio > 0.008), the strong complexation of citrate completely inhibited the formation of lepidocrocite, resulting in a noncrystalline Fe oxide precipitate.

SUMMARY AND CONCLUSIONS

The results of the present investigation indicate the role of citrate, one of the most common organic ligands in natural environments, in retarding the kinetics of Fe(II) oxidation and the resultant Fe(III) hydrolysis. The retardation of Fe(II) oxidation apparently led to the inhibition of the nucleation of goethite and the promotion of the crystal growth of lepidocrocite especially at a citrate/Fe molar ratio of about 0.001. The presence of citrate appeared to influence the oxygen coordination and the way that the edge-sharing Fe(O,OH)$_6$ octahedra were linked together during the crystallization and promoted the formation of lepidocrocite. Further increase in the amounts of citrate distorted the structural order, resulting in the increasing inhibition of the crystal growth of lepidocrocite and the formation of noncrystalline Fe oxides at citrate/Fe molar ratio of 0.01.

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