EFFECT OF SILICA POLYMERIZATION ON THE OXALATE-PROMOTED DISSOLUTION OF GOETHITE

MATTHEW J. EICK[1],*, TODD P. LUXTON[2], AND HOLLY A. WELSH[1]

[1] Department of Crop and Soil Environmental Sciences, Virginia Tech, Blacksburg, VA 24061, USA

[2] U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, 5995 Center Hill Ave, Cincinnati, OH 45224, USA

Abstract—Numerous studies have investigated the ligand-promoted dissolution of Fe (oxyhydr)oxides. In natural environments, inorganic ligands can compete with organic ligands for surface sites on (oxyhydr)oxides which may influence dissolution rates. Published research of this interaction and its effect on the dissolution of (oxyhydr)oxides is rare. The objective of the present study was to examine the extent to which silica, as a naturally occurring competitive ligand added in the form of silicic acid, impacts the oxalate-promoted dissolution of the common soil Fe (oxyhydr)oxide goethite. Sorbed silica reduced the oxalate-promoted dissolution rate of goethite at all surface coverages investigated. As initial silica solution concentrations increased from 0.50 mM to 5.0 mM, relatively little change in the dissolution rate was observed. Fourier-transform infrared (FTIR) spectra indicated that, as silica-surface coverages increased, the silica underwent polymerization on the goethite surface. Initially, silicate was associated with surface functional groups, but as polymerization occurred some of the silica appeared to desorb from the goethite surface without being released into the bulk solution, suggesting that silica polymers formed discrete islands or surface clusters that grew away from the goethite surface rather than expanding epitaxially across the surface. Minimal changes were observed in the quantity of reactive goethite surface, which is responsible for the observed dissolution rates, as silica-surface coverages increased.

Key Words—Adsorption, Dissolution, Goethite, Oxalate, Polymerization, Silicic Acid.

INTRODUCTION

Naturally occurring organic ligands are ubiquitous in soil rhizosphere environments and may serve as detoxifying agents, increase the solubility of nutrients, or may be metabolic by-products. The ligand-promoted dissolution of Fe (oxyhydr)oxides and their importance in the geochemical cycling of Fe has been examined extensively (Cambell and Eick, 2002; Stumm 1997; Nowack and Sigg, 1996; Biber *et al.*, 1994; LaKind and Stone, 1989; Zinder *et al.*, 1986). The dissolution of Fe (oxyhydr)-oxides in the presence of both plant and bacterial siderophores has been the focus of recent studies (Mikutta and Kretzschmar, 2008; Reichard *et al.*, 2007; Reichard *et al.*, 2005; Kraemer *et al.*, 2005; Borer *et al.*, 2005; Cheah *et al.*, 2003; Cervini-Silva and Sposito, 2002; Holmen *et al.*, 1999; Holmen and Casey, 1996). Siderophores are compounds that have a very high affinity for ferric (Fe^{3+}) iron and are important for Fe nutrition of plants and microorganisms under Fe-limiting conditions. For example, Inoue (1993) and Hiradate and Inoue (1998) examined the dissolution of Fe (oxyhydr)-oxides by phytosiderophores at circum-neutral pH values and observed significant Fe dissolution for ferrihydrite but not for goethite. Those authors proposed that the crystallinity of the Fe (oxyhydr)oxide affects the extent of

dissolution, with the more crystalline Fe (oxyhydr)oxides such as goethite being resistant to phytosiderophore-promoted dissolution. In recent studies, the dissolution of goethite in the presence of the phytosiderophore 2'-deoxymugeneic acid (DMA) and aliphatic organic acids was examined (Reichard *et al.*, 2005, 2008); the organic acids were found to have had a synergistic effect on the steady-state dissolution of goethite by DMA. In addition, under non-steady state conditions, a fast dissolution step was triggered by the organic acid. They proposed that organic acid created a kinetically liable pool of Fe at the goethite surface which was rapidly released upon the addition of the phytosiderophore.

Understanding the ligand-promoted dissolution of Fe (oxyhydr)oxide minerals is neessary in order to better understand Fe bioavilability and cycling in natural systems. Most studies examining ligand-promoted dissolution, however, have focused primarily on elucidating dissolution mechanisms in the presence of one or two organic ligands. In natural soil rhizosphere environments, organic ligands will compete with metal cations, oxyanions, and numerous organic ligands for reactive surface sites on Fe (oxyhydr)oxides. Depending on the nature of the adsorptive species, the pH of the soil environment, and the type of surface complex formed, organic ligand-promoted dissolution may either be inhibited or enhanced (Reichard *et al.*, 2005; Campbell and Eick, 2002; Eick *et al.*, 1999). For example, inorganic oxyanions, such as arsenate, form strong surface complexes with oxide surfaces and have been observed to inhibit the oxalate-

promoted dissolution of goethite (Eick et al., 1999). Those reactions may reduce siderophore-promoted dissolution of Fe (oxyhydr)oxides and influence the Fe availability for plants and microorganisms.

Unlike arsenic, silica, as silicic acid, is ubiquitous in terrestrial environments. Silicic acid, like arsenate, has a high affinity for Fe (oxyhydr)oxide surfaces (Sigg and Stumm, 1981; Vempati and Loeppert, 1989; Vempati et al., 1990; Hansen et al., 1994a, 1994b; Doelsch et al., 2001, 2003). Furthermore, it is commonly present in soils and natural waters at concentrations from 5 to 35 mg L^{-1} (0.17–1.24 mM) and not infrequently at concentrations as high as 75 mg L^{-1} (2.7 mM) in groundwater (Iller, 1979). In addition to strong surface complexation with Fe (oxyhydr)oxide surfaces, silicic acid has been shown to form polymers at surface coverages of <1 monolayer (Vempati et al., 1990; Hansen et al., 1994b; Doelsch et al., 2001; 2003; Luxton et al., 2008). Silicic acid may, therefore, have a significant effect on the organic ligand-promoted dissolution of Fe (oxyhydr)oxides and on Fe acquisition by plants and microorganisms.

MATERIAL AND METHODS

Characterization of goethite

Goethite used in the current study was synthesized by hydrolysis of ferric nitrate (Fe(NO$_3$)$_3$) using a method described by Schwertmann and Cornell (1991). All solutions were prepared with distilled doubly-deionized water (18.2 M.Ω-cm) and reagent-grade chemicals. Contact with glass surfaces was avoided to prevent silica contamination. The identity, purity, and structure of the goethite sample was confirmed by X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and field emission scanning electron microscopy (FESEM). Results from these analyses were consistent with data presented by Schwertmann and Cornell (1991, 1996) and a goethite standard from Bayer® (Krefeld, FRG). The FESEM images showed that the synthetic goethite consisted of euhedral acicular crystals of uniform shape and size, ~300 nm long and 75 nm wide. The quantity of poorly crystalline or amorphous Fe was determined by the ratio of ammonium oxalate (AO), in the dark, to citrate-bicarbonate-dithionite (CBD)-extractable Fe (Loeppert and Inskeep, 1996; Schwertmann and Cornell, 1991). The extractable Fe was 0.28% (AO Fe mg/CBD Fe mg), indicating minimal amounts of amorphous or short-ordered crystals. The specific surface area was 76 m^2 g^{-1}, as determined by a five-point N$_2$ Brunauer-Emmett-Teller (BET) gas adsorption isotherm. The point of zero charge as determined by the isoelectric point (IEP) was 9.56.

Adsorption envelopes

Oxalate adsorption envelopes as a function of pH were obtained at various oxalate concentrations using a a

pH-monitored, stirred-batch reactor technique in a 0.01 M NaCl background electrolyte with a goethite suspension density of 5 g L^{-1}. The adsorption profiles were measured in triplicate from pH 3 to 10. An appropriate quantity (2.0 g) of freeze-dried and N$_2$-sparged goethite was weighed into a 500 mL Teflon reaction vessel to which 350 mL of 0.01 M NaCl was added. The suspension was dispersed for ~2 min using an ultrasonic dismembrator (Fisher Scientific, Atlanta, GA, USA). The Teflon liner was placed in a water-jacketed reaction vessel kept at 25ºC, stirred at 300 rpm using a three-blade impeller, and kept under positive pressure with N$_2$ gas to eliminate the CO$_2$ effects. All batch reactors were made of amber glass and thoroughly wrapped with Al-foil to exclude light. The suspension was allowed to hydrate for a period of 24 h while the pH was adjusted to 10 using a Brinkman® 716 Stat-Trino pH stat (Brinkman Instruments, Westbury, NY) with either 0.1 M HCl or NaOH.

After the 24 h hydration period, the suspension was brought to volume (400 mL) minus the quantity of oxalate stock solution to be added. The oxalate was added from a 0.1092 M sodium oxalate stock solution kept in an amber bottle, in the dark, to prevent photo-oxidation. The suspension was allowed to equilibrate for 3 h after which a 10 mL sample was removed carefully from the stirred-batch reactor, using an electronic pipette, and filtered through a 0.10 µm filter (Gelman Sciences, Ann Arbor, Michigan, USA) into an acid-washed polypropylene test tube. After each sampling event, the pH in the reaction vessel was reduced by one unit using 0.1 M HCl and allowed to re-equilibrate for 3 h. Oxalate-solution concentrations were analyzed using a Sievers 900 (Ionics Instruments, Boulder, Colorado, USA) total organic carbon analyzer.

Silicic acid adsorption profiles were obtained for initial concentrations of 0.5 mM, 2.5 mM, and 5.0 mM using a batch technique in individual 250 mL polycarbonate bottles, using the same NaCl background and goethite suspension density as for oxalate. All adsorption measurements were obtained in duplicate from pH 3 to 11. Individual batch experiments were chosen for silicic-acid adsorption over the pH-monitored, stirred-batch technique due to the required extension of equilibration time to 40 h (Waltham and Eick, 2002; Luxton et al., 2008). Prior to sealing, each bottle was adjusted to the appropriate pH value followed by 5 min of sparging with N$_2$. Bottles were then sealed and placed in an Innova 4230 (New Brunswick Scientific Edison, New Jersey, USA) refrigerated incubator shaker at 300 rpm and 25ºC. The pH was checked and readjusted three times daily during equilibration, and each sample sparged with N$_2$ for 5 min prior to resealing. Fluctuations in the pH were minimal (<0.1) after 30 h. After the 40 h equilibration time period the pH was measured and a 10.00 mL sample was removed from the reaction vessel and analyzed using an inductively

coupled plasma atomic emission spectrometer (ICP-AES) (SpectroFlame FTMOA85D, Spectro Analytical Instruments, Fitchburg, Massachusetts, USA).

Oxalate adsorption was investigated in the presence of sorbed silica as a function of silica concentration at pH values of 3, 4, 5, and 6 using the same batch procedure as above. After the 40 h equilibration period, an appropriate quantity of pH-adjusted oxalate, to achieve a solution concentration of 5 mM, was added to the batch reactors from a 0.1092 M stock solution and the pH was adjusted manually using 0.10 M NaOH. The pH was monitored over 3 h and was adjusted as necessary. After the 3 h equilibration period, a 10 mL sample was removed carefully from the batch reactor, using an electronic pipette, and filtered through a 0.10 μm metrical membrane (Gelman Science, Ann Arbor, Michigan, USA) into an acid-washed polypropylene test tube and analyzed using a total organic carbon analyzer.

Dissolution experiments

All of the dissolution studies were conducted in the presence of 5.0 mM oxalate using a pH-monitored, stirred-batch reactor technique in 0.01 M NaCl background electrolyte with a goethite suspension density of 5 g L^{-1}. Dissolution experiments were conducted in duplicate at pH values 3, 4, 5, and 6. Greater pH values were not investigated because previous research had demonstrated negligible goethite dissolution at pH >6 (Eick *et al.*, 1999). Dissolution experiments were carried out using the same procedure as the adsorption envelopes where silica was added to the hydrated goethite and allowed to equilibrate for 40 h before addition of the oxalate. At appropriate times, a 10 mL sample was extracted carefully from the stirred-batch reactor, using an electronic pipette, and filtered through a 0.10 μm metrical membrane into an acid-washed polypropylene test tube and analyzed for silica and Fe using ICP-AES. All dissolution experiments were conducted for 50 h and dissolution rates were calculated form linear regression of the dissolution curve after 10−15 h.

FTIR spectroscopy

Fourier-transform infrared (FTIR) spectra were generated for samples collected for silicate adsorption on goethite as a function of reaction time, silicate concentration, and pH. The FTIR spectra were obtained using a Thermo Nicloet Nexus® 670 spectrometer and a horizontal Thermo Nicolet Smart ARK ATR attachment, equipped with a 45º ZnSe trapezoidal crystal with 12 internal reflections and a cutoff of 600 cm^{-1} (Thermo Electron, Madison Wisconsin, USA). The measured path length was ~12 μm, based on the molar absorptivity of water. The spectrometer was equipped with a KBr beam splitter and a DTGS detector. The experimental procedure for preparing IR samples followed the same procedure described for the adsorption envelopes with the following modifications. After 6 and 48 h, a 25 mL sample was removed from the reaction vessel for FTIR analysis. The sample was filtered onto a 0.22 μm membrane filter. The resulting goethite was then washed with 25 mL of 0.01 M NaCl to remove entrained, non-reacted silicate prior to IR analysis. The wet goethite paste was smeared onto the ZnSe crystal and analyzed immediately. Spectra were obtained from the co-addition of 512 scans collected at a resolution of 4 cm^{-1}. Data analysis of the collected spectrum was performed using the *Omnic* software package (Version 7.2, 2005, Thermo Scientific, Waltham, Massachusetts, USA). All of the spectra were corrected for the presence of water. In addition, a spectrum of unreacted goethite (prepared under the same conditions) was subtracted from the goethite + silicate spectrum in order to evaluate the adsorbed silica species only. After the goethite subtraction, the resulting spectra were baseline corrected between 1400 and 700 cm^{-1} using a linear function.

RESULTS AND DISCUSSION

Adsorption envelopes

Oxalate and silica exhibited contrasting adsorption behaviors on goethite over the range in solution concentrations investigated (Figure 1). The differences in the adsorption envelopes can be related to the difference between the pK$_a$ values of silicic and oxalic acid. Typically, the adsorption of weak acids is maximized at a pH near the first acid dissociation constant or pK$_1$ value of the protonated form of the adsorbing anion (McBride, 1994). Oxalate (pk$_1$ = 1.23) exhibited maximum adsorption at low pH values while silica (pk$_1$ = 9.46) exhibited maximum adsorption at a
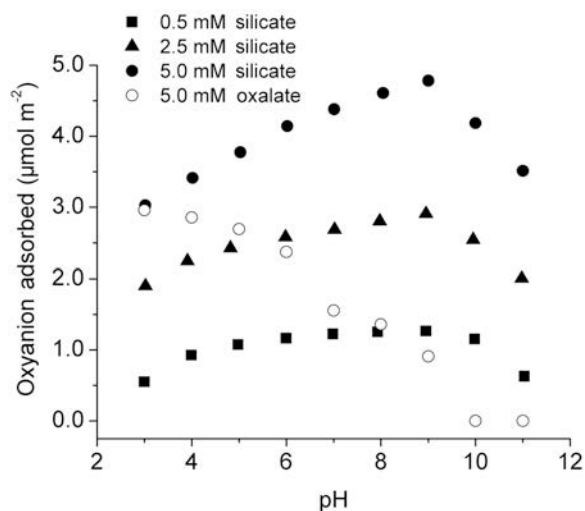

Figure 1. Silicate and oxalate adsorption on goethite as a function of pH. Goethite suspension density: 5 g L^{-1}; background electrolyte: 0.10 M NaCl.

pH value of ~9, results which were consistent with other investigations examining oxalate and silica adsorption on goethite (Swedlund and Webster, 1999; Eick *et al.*, 1999; Gustafsson, 2001; Glover *et al.*, 2002; Waltham and Eick, 2002). Based on reactive surface site density of 5.85 µmol sites nm^{-2} (Barrón and Torrent, 1996) and the formation of a bidentate surface complex for both oxalate and silica, monolayer surface coverages were only exceeded at the 5.0 mM silica concentration, suggesting the formation of surface polymers at this concentration (Figure 1). This is consistent with literature which has demonstrated that, at similar surface loadings, silica forms surface polymers on Fe (oxyhydr)-oxide surfaces (Vempati *et al.*, 1994b; Doelsch *et al.*, 2001, 2003).

Oxalate adsorption in the presence of sorbed silicic acid was reduced at all concentrations investigated (Figure 2). Furthermore, the reduction in oxalate adsorption increased with an increase in pH. The greatest reduction in oxalate adsorption occurred at the 0.50 mM silicic acid concentration which ranged from 18% to 63% at pH 3 and 6, respectively. A further reduction in oxalate adsorption occurred as silica concentration increased from 0.50 mM to 2.5 mM for all pH values investigated except pH 6. Oxalate adsorption was reduced from 33% to 72% at pH values of 3 and 5, respectively, results which are consistent with the adsorption behavior of oxalate and silicic acid as a function of pH. A further increase in silica from 2.5 to 5.0 mM resulted, however, in minimal changes in the quantity of oxalate sorbed to the goethite surface suggesting that at greater silicate-surface coverages, excess reactive functional groups existed for sorption of oxalate indicating that silicate does not adsorb to the goethite surface as a monomeric species only (*i.e.* formation of surface polymers).
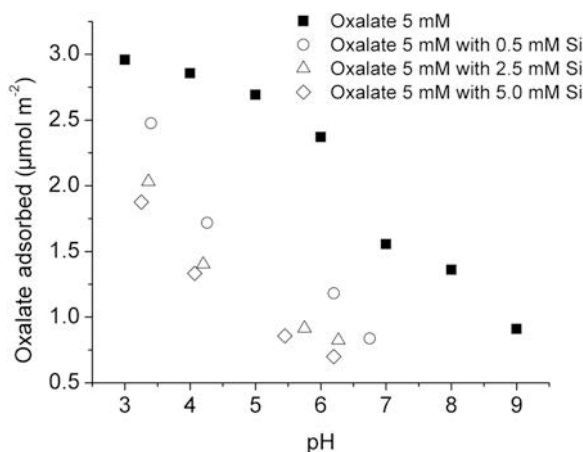
FTIR spectroscopy

The adsorption of silicate was further investigated to determine changes in the bonding environment as a function of surface concentration and the impact changes in bonding may have had on oxalate adsorption. Previous studies demonstrated that silicic acid adsorbs quickly in the first 8 h, followed by a much slower adsorption rate after 36 h (Luxton *et al.*, 2008; Waltham and Eick, 2002). Spectra were, therefore, collected at 6 and 48 h to evaluate the changes in the speciation of adsorbed silicate and the adsorption mechanism as a function of time. The primary IR region of interest was located between 1300 and 900 cm^{-1}, an area associated with Fe−O−Si linkages (970−930 cm^{-1}), Si−OH linkages (960−1000 cm^{-1}), and asymmetric Si−O−Si stretching vibrations (1080 and 1150 cm^{-1}) (Chaneac *et al.*, 1996; Della Volpe *et al.*, 1997; Doelsch *et al.*, 2001, 2003; Hansen *et al.*, 1994b; Mul *et al.*, 2004; Parfitt *et al.*, 1992; Vempati and Loeppert, 1989). Spectra collected at pH 4 and 6 at two time intervals (6 h and 48 h) (Figures 3 and 4; Curves a correspond to 0.50 µM Si and Curves b to 5.0 µM) indicate that silicate does polymerize on goethite and that silicate polymerization is related to both concentration and pH, as clearly seen by the appearance of Si−O−Si stretching vibrations between 1080 and 1150 cm^{-1} after 48 h. The broad absorption peaks associated with silicate are probably

Figure 2. Oxalate **adsorption** on goethite in the presence of **sorbed** silicate as a function of pH. Goethite suspension density: 5 g L^{-1}; background electrolyte: 0.10 M NaCl.
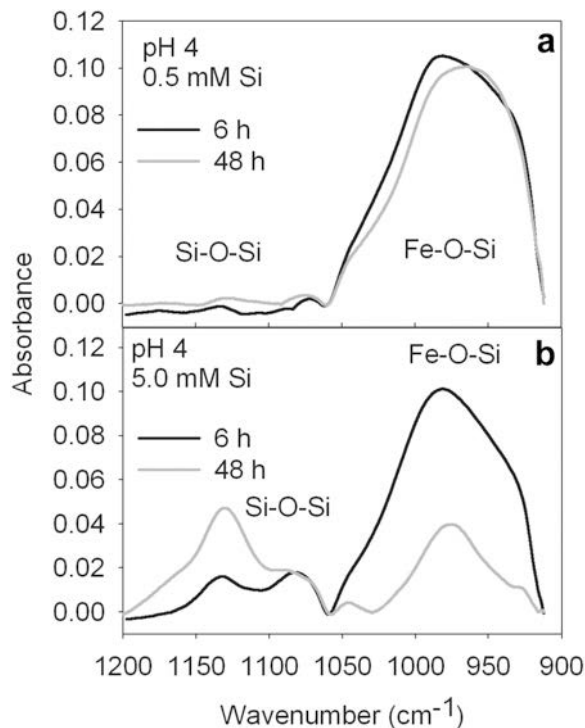

Figure 3. FTIR spectra of silicate sorbed on goethite after 6 and 48 h at pH 4: (a) initial silicate concentration of 0.50 mM; and (b) initial silicate concentration 5.0 mM.

related to the disordered nature and size of the silica polymers resulting from changes in goethite surface morphology (Alverez and Sparks, 1985). After 48 h, the presence of silicate polymers was detected based on the appearance of absorption bands between 1080 and 1150 cm^{-1}, indicting a change in the silicate adsorption mechanism with time, since adsorption was no longer isolated on the goethite surface. The FTIR spectra indicate that silicate initially adsorbed to the goethite surface as a monomer or possibly a dimer (Alverez and Sparks, 1985) before undergoing further polymerization. Adsorption and FTIR data demonstrate that the mechanism controlling silicate polymerization was related to the surface concentration of silicate. At low surface concentrations, only minimal quantities of silica polymers were formed (pH 4 and 6, 0.50 μM silicate), and the majority of the adsorbed silicate was primarily associated with surface functional groups (Fe−O−Si) and not polymers as shown by peak maxima between 950 and 1000 cm^{-1}. The 5.0 μM data suggested a change in the silicate surface speciation with time. Initially, silicate was associated with surface functional groups, but as polymerization took place, some of the silica appears to have desorbed from the goethite surface without being released into the bulk solution, as can be seen readily through the decrease in the intensity of the Fe−O−Si and Si−OH peaks and the increase in the intensity of the Si−O−Si peaks between 6 and 48 h

(Figures 3 and 4). Silica polymers formed discrete islands or surface clusters, which grew away from the goethite surface rather than expanding epitaxially across the surface. Such results were not unexpected, based on the difference in the Si−O ($\approx$1.61 Å) and Fe−O ($\approx$1.97 Å) bond lengths. Similar results were observed by Fendorf *et al.* (1996) who examined the surface morphology of hydrous chromium oxide (HCO) precipitates on colloidal silica and goethite. Based on these results and the extent of lateral growth of the silica polymers, one would expect minimal change in the quantity of unreacted goethite that would be available for oxalate-promoted dissolution.

Dissolution studies

Goethite dissolution was reduced in the presence of sorbed silica at all pH values investigated (Figure 5, Table 1). This was not unexpected based on the reduction in oxalate adsorption and previous investigations showing an inhibition in oxalate-promoted dissolution of goethite in the presence of specifically adsorbed oxyanions (Eick *et al.*, 1999). At pH values 3 and 4, a further increase in the surface concentration of silica had a negligible effect on the oxalate-promoted dissolution of goethite (Figure 5, Table 1). One would expect similar results at pH values of 5 and 6 based on the oxalate-adsorption behavior in the presence of sorbed silica (Figure 2). In addition to measuring Fe and oxalate release as a function of time, dissolved silicic acid concentrations were also measured (data not shown). At 0.50 mM, the silicic acid solution concentrations increased as a function of time. However, at 2.5 and 5.0 mM, the solution concentrations of silicic acid remained essentially constant over the course of the dissolution experiment, consistent with FTIR results which found mainly sorbed monomers or dimers of
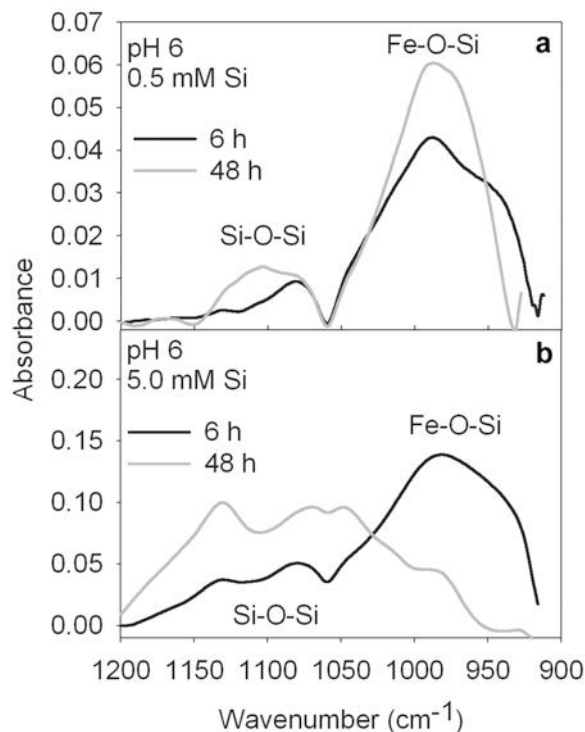

Figure 4. FTIR spectra of silicate sorbed on goethite after 6 and 48 h at pH 6: (a) initial silicate concentration of 0.50 mM; and (b) initial silicate concentration of 5.0 mM.
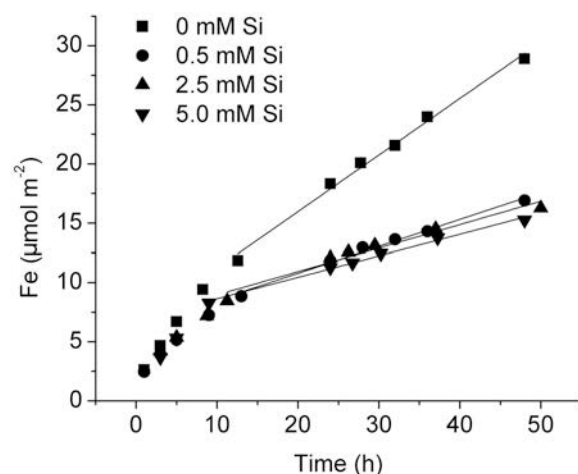

Figure 5. Oxalate-promoted dissolution of goethite at pH 3 as a function of sorbed silicate. Goethite suspension density: 5 g L^{-1}; background electrolyte 0.10 M NaCl.

Table 1. Ligand-promoted dissolution rates of goethite by oxalate in the presence and absence of silica at pH 3, 4, 5, and 6.

pH	Initial Si concentration (mM)	Dissolution rate (mol m^{-2} h^{-1})	Correlation of determination (r^2)
3	0.0	49.4×10^{-8}	99
	0.5	22.6×10^{-8}	98
	2.5	19.7×10^{-8}	99
	5.0	18.7×10^{-8}	99
4	0.0	30.1×10^{-8}	99
	0.5	15.4×10^{-8}	99
	2.5	15.0×10^{-8}	99
	5.0	11.0×10^{-8}	98
5	0.0	9.82×10^{-8}	99
	0.5	4.56×10^{-8}	97
6	0.0	0.29×10^{-8}	99
	0.5	0.10×10^{-8}	76

silicic acid at 0.50 mM and mainly polymers at greater concentrations. Based on the FTIR results and on silicic-acid release, as silica concentrations increased, polymers formed on the goethite surface with the morphology of discrete islands or clusters which grew away from the goethite surface. Unreacted goethite surface was still available for oxalate adsorption, which resulted in a negligible decrease in the dissolution rates as the surface concentration of the silica increased.

These interpretations are, however, inconsistent with the reduction in oxalate adsorption observed as silica concentrations increased from 0.50 mM to 2.5 mM (Figure 2). As ligand-promoted dissolution of oxides was a surface-controlled phenomenon, one should observe a decrease in the dissolution rate as oxalate adsorption decreased (Zinder et al., 1986). Persson and Axe (2005) examined the adsorption of oxalate on goethite using FTIR spectroscopy and demonstrated conclusively that oxalate forms both inner- and outer-sphere surface complexes and that those complexes coexist over a broad pH range. An increase in the outer-sphere complex as pH increased was also observed by those authors. Specific adsorption of oxyanions such as silica with protolyzable functional groups often results in a decrease in the surface charge of the oxide minerals (Anderson and Malotky, 1979). For silica, such a decrease in surface charge was greater as pH increased (Luxton et al., 2006). The assertion here is, therefore, that silica polymers reduced the adsorption of outer-sphere oxalate complexes due to a combination of electrostatic repulsion and steric interactions as silica sorption changed from a monomer to a polymer. This proposed mechanism is consistent with the experimental results which show an increase in the reduction of oxalate adsorption as pH increased (i.e. a greater ratio of outer- to inner-sphere complexation) and a greater decrease in the goethite surface charge after silica adsorption as the pH increased (Luxton et al., 2006). Although oxalate adsorption was reduced as silica

adsorption increased, this is primarily associated with outer-sphere oxalate complexes which are not dissolution enhancing.

CONCLUSIONS

The oxalate-promoted dissolution of goethite was reduced in the presence of sorbed silica at all pH values investigated. Increases in sorbed silica had a negligible effect on dissolution rates. The results from FTIR spectroscopy demonstrate that as surface coverage of silica increases, surface complexes change from monomers to polymers. The morphology of these polymers is likely to be surface clusters or islands which grow away from the surface leaving unreacted goethite available for oxalate-promoted dissolution, resulting in a negligible decrease in the dissolution rate as silica surface coverage increases. Although oxalate adsorption decreases as silica surface coverage increases, this decrease is probably associated with outer-sphere surface complexes which do not promote goethite dissolution. In addition to inhibiting ligand-promoted dissolution of goethite, silica polymers coat and block adsorption sites which may have a profound effect on the potential bioavailability of nutrients and contaminants. In natural systems, silica may play a critical role in the acquisition of Fe by both plants and microbes by reducing dissolution of Fe-bearing minerals.

REFERENCES

Alverez, R. and Sparks, D.L. (1985) Polymerization of silicate anions in solutions at low concentrations. Nature, 318, 649−651.

Anderson, M.A. and Malotky, D.T. (1979) The adsorption of protolyzable anions in hydrous oxides at the isoelectric pH. Journal of Colloid and Interface Science, 72, 413−427.

Barrón, V. and Torrent, J. (1996) Surface hydroxyl configuration of various crystal faces of hematite and goethite. Journal of Colloid and Interface Science, 177, 407−410.

Biber, M.V., Dos Santos Afonso, M., and Stumm, W. (1994) The coordination chemistry of weathering: IV: Inhibition of the dissolution of oxide minerals. *Geochimica et Cosmochimica Acta*, **58**, 1999−2010.

Borer, P.M., Sulzberger, B., Reichard, P., and. Kraemer, S.M. (2005) Effect of siderophores on the light-induced dissolution of colloidal iron(III) (hydr)oxides. *Marine Chemistry*, **93**, 179−193.

Campbell, J.L. and Eick, M.J. (2002) Effects of oxyanions on the EDTA-promoted dissolution of goethite. *Clays and Clay Minerals*, **50**, 336−341.

Cervini-Silva, J. and Sposito, G. (2002) Steady-state dissolution kinetics of aluminum-goethite in the presence of desferrioxamine B and oxalate ligands. *Environmental Science and Technology*, **36**, 337−342.

Chaneac, C., Tronc, E., and Jolivet, J.P. (1996) Magnetic iron oxide-silica nanocomposites. Synthesis and characterization. *Journal of Materials Chemistry*, **6**, 1905−1911.

Cheah, S.F., Kraemer, S.M., Cervini-Silva, J., and Sposito, G. (2003) Steady-state dissolution kinetics of goethite in the presence of desferrioxamine B and oxalate ligands: implications for microbial acquisition of iron. *Chemical Geology*, **198**, 63−75.

Della Volpe, C., Dire, S., and Pagani, E. (1997) A comparative analysis of surface structure and surface tension of hybrid silica films. *Journal of Noncrystalline Solids*, **209**, 51−60.

Doelsch, E., Stone, W.E.E., Petit, S., Masion, A., Rose, J., Bottero, J.Y., and Nahon, D. (2001) Speciation and crystal chemistry of Fe(III) chloride hydrolyzed in the presence of SiO_4 ligands. 2. Characterization of Si-Fe aggregates by FTIR and Si-29 solid-state NMR. *Langmuir*, **17**, 1399−1405.

Doelsch, E., Masion, A., Rose, J., Stone, W.E.E., Bottero, J.Y., and Bertsch, P.M. (2003) Chemistry and structure of colloids obtained by hydrolysis of Fe(III) in the presence of SiO_4 ligands. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **217**, 121−128.

Eick, M.J., Peak, J.D., and Brady, W.D. (1999) The effect of oxyanions on the oxalate promoted dissolution of goethite. *Soil Science Society of America Journal*, **63**, 1133−1144.

Fendorf, S.E., Li, G., and Gunter, M.E. (1996) Micromorphologies and stabilities of chromium(III) surface precipitates elucidated by scanning force microscopy. *Soil Science Society of America Journal*, **60**, 99−106.

Glover, L.J., Eick, M.J., and Brady, P.V. (2002) Influence of residence time and organic acids on the desorption kinetics of Cd^{2+} and Pb^{2+} from goethite. *Soil Science Society of America Journal*, **66**, 797−804.

Gustafsson, J.P. (2001) Modeling competitive anion adsorption on oxide minerals and an allophane soiling soil. *European Journal of Soil Science*, **52**, 639−653.

Hansen, H.C.B., Rabenlange, B., Raulundrasmussen, K., and Borggaard, O.K. (1994a) Monosilicate adsorption by ferrihydrite and goethite at pH 3−6. *Soil Science*, **158**, 40−46.

Hansen, H.C.B., Wetche, T.P., Raulund-Rasmussen, K., and Borggaard, O.K. (1994b) Stability constants for silicate adsorbed to ferrihydrite. *Clay Minerals*. **29**, 341−350.

Hiradate, S. and Inoue, K. (1998) Dissolution of iron from iron (hydr)oxides by mugineic acid. *Soil Science and Plant Nutrition*, **44**, 305−313.

Hochella, Jr, M.F. (1990) Atomic structure, microtopography, composition, and reactivity of mineral surfaces. Pp. 87−128 in: *Mineral-Water Interface Geochemistry* (M.F. Hochella, Jr and A.F. White, editors). Reviews in Mineralogy, **23**, Mineralogical Society of America, Washington, D.C.

Holmen, B.A. and Casey, W.H. (1996) Hydroxamate ligands, surface chemistry, and the mechanism of ligand-promoted dissolution of goethite. *Geochimica et Cosmochimica Acta*, **60**, 4403−4416.

Holmen, B.A., Sison, J.D., Nelson, D.C., and Casey, W.H. (1999) Hydroxamate siderophores, cell growth and Fe(III) cycling in two anaerobic iron oxide media containing Geobacter metallireducens. *Geochimica et Cosmochimica Acta*, **63**, 227−239.

Inoue, K., Hiradate, S., and Takagi, S. (1993) Interaction of mugineic acid with synthetically produced iron-oxides. *Soil Science Society of America Journal*, **57**, 1254−1260.

Iller, R.K. (1979) *The Chemistry of Silica*. Jon Wiley & Sons, New York.

Kraemer, S.M., Butler, A., Borer, A.P., and Cervini-Silva, J. (2005) Siderophores and the dissolution of iron-bearing minerals in marine systems. *Molecular Geomicrobiology*, **59**, 53−84.

LaKind, J. and Stone, A.T. (1989) Reductive dissolution of goethite by phenolic reductants. *Geochimica et Cosmochimica Acta*, **58**, 1999−2010.

Loeppert, R.L. and Inskeep, W.P. (1996) Iron. Pp. 639−664 in: *Methods of Soil Analysis, Part 3* (D. L. Sparks, editor). SSSA Book Series No. **5**, Soil Science Society of America, Madison, Wisconsin, USA.

Luxton, T.P., Tadanier, C.J., and Eick, M.J. (2006) Competitive adsorption of arsenite and silicic acid on goethite. *Soil Science Society of America*, **70**, 204−214.

Luxton, T.P., Eick, M.J., and Rimstidt, J.D. (2008) Kinetics of the competitive adsorption of arsenite and silicic acid on goethite. *Chemical Geology*, **252**, 125−135.

McBride, M.B. (1994) *Environmental Chemistry of Soils*. Oxford University Press, New York. 139 pp.

Mikutta, C. and Kretzschmar, R. (2008) Synthetic coprecipitates of exopolysaccharides and ferrihydrite. Part II: Siderophore-promoted dissolution. *Geochimica et Cosmochimica Acta*, **72**, 1128−1142.

Mul G., Hamminga, G.M., and Moulijn J.A. (2004) Operando ATR-FTIR analysis of liquidphase catalytic reactions: can heterogeneous catalysts be observed? *Vibrational Spectroscopy*, **34**, 109−121.

Nowack, B. and Sigg, L. (1996) Adsorption of EDTA and metal-EDTA complexes on goethite. *Journal of Colloid and Interface Science*, **177**, 106−121.

Parfitt, R.L., Vandergaast, S.J., and Childs, C.W. (1992) A structural model for natural siliceous ferrihydrite. *Clays and Clay Minerals*, **40**, 675−681.

Persson, P and Axe, K. (2005) Adsoprtion of oxalate and malonate at the water-goethite interface: molecular surface speciation from IR spectroscopy. *Geochimica et Cosmochimica Acta*, **69**, 541−552.

Reichard, P.U., Kraemer, S.M., Frazier, S.W., and Kretzschmar, R. (2005) Goethite dissolution in the presence of phytosiderophores: rates, mechanisms, and the synergistic effect of oxalate. *Plant and Soil*, **276**, 115−132.

Reichard, P.U., Kretzschmar, R., and. Kraemer, S.M. (2007) Dissolution mechanisms of goethite in the presence of siderophores and organic acids. *Geochimica et Cosmochimica Acta*, **71**, 5635−5650.

Schwertmann, U. and Cornell, R.M. (1991) *Iron Oxides in the Laboratory: Preparation and Characterization*. VCH, Weinheim, Germany.

Schwertmann, U. and Cornell, R.M. (1996) *The Iron Oxides: Structures, Properties, Reactions, Occurrences and Uses.* VCH, Weinheim, Germany.

Sigg, L. and Stumm, W. (1981) The interaction of anions and weak acids with the hydrous goethite (?-FeOOH) surface. *Colloids and Surfaces*, **2**, 101−117.

Stumm, W. (1997) Reactivity at the mineral-water interface: dissolution and inhibition. *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, **120**, 143−166.

Swedlund, P.J., and Webster, J.G. (1999) Adsorption and polymerization of silicic acid on ferrihydrite, and its effect

on arsenic adsorption. *Water Resources Journal*, **33**, 3413−3422.

van der Marel, H.W. and Beutelspacher, H. (1976) *Atlas of Infrared Spectroscopy of Clay Minerals and their Mixtures*. Elsevier, New York, 326 pp.

Vempati, R.K. and Loeppert, R.H. (1989) Influence of structural and adsorbed Si on the transformation of synthetic ferrihydrite. *Clays and Clay Minerals*, **37**, 273−279.

Vempati, R.K., Loeppert, R.H., Dufner, D.C., and Cocke, D.L. (1990) X-ray photoelectron spectroscopy as a tool to differentiate silicon-bonding state in amorphous iron oxides.

Soil Science Society of America Journal, **54**, 695−698.

Waltham, C. and Eick, M.J. (2002) Kinetics of arsenic adsorption on goethite in the presence of sorbed silicic acid. *Soil Science Society of America Journal*, **66**, 818−825.

Zinder, B.G., Furrer, G., and Stumm, W. (1986) The coordination chemistry of weathering. II. Dissolution of Fe(III) oxides. *Geochimica et Cosmochimica Acta*, **50**, 1861−1869.