The Influence of Oxyanions on the EDTA-promoted

Dissolution of Goethite

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Thesis submitted to the Faculty of

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

IN

CROP AND SOIL ENVIRONMENTAL SCIENCE

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May 1, 2001

Blacksburg, VA

Keywords: dissolution, adsorption, goethite, EDTA, phosphate, selenite, molybdate

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ABSTRACT

Organic ligands, such as EDTA, accelerate the dissolution of silicate and oxide minerals. In natural systems oxyanions can compete with organic ligands for mineral surface sites thereby affecting ligand-promoted dissolution rates. Oxyanions can either enhance or inhibit dissolution depending upon pH. It has been suggested that the type of surface complex formed by the oxyanion is responsible for differences in ligand-promoted dissolution rates with mononuclear being dissolution enhancing and bi- or multinuclear being dissolution inhibiting. However, recent research has demonstrated that the type of surface complex formed by the oxyanion is not responsible for differences in ligand-promoted dissolution rates of oxide minerals. Accordingly, this manuscript examines the influence of selenite, molybdate, and phosphate on the EDTA-promoted dissolution of goethite and proposes a mechanism for the observed differences in dissolution rates over a pH range of 4 - 8. We propose that the surface complex formed by EDTA is the controlling factor for the observed dissolution rate, with mononuclear EDTA surface complexes accelerating goethite dissolution compared to bi- or multinuclear complexes. These experimental results suggest that EDTA forms multinuclear complexes with goethite surfaces at pH values ≥ 6 and mononuclear complexes with goethite surfaces at pH values < 6. Dissolution results show that when the oxyanion and the EDTA are present in the system at concentrations nearly equaling the surface sites available for adsorption, the oxyanion reduces the adsorption of EDTA and inhibits dissolution over the pH range of 4 - 8.

However, a different mechanism occurs at pH values ≥ 6 when the oxyanion is present at 0.1 mM. EDTA adsorbs but the number of carboxylic groups that can sorb to the surface is reduced causing the formation of mononuclear complexes. This shift from multi- to mononuclear surface complexes enhances the EDTA-promoted dissolution of goethite in the presence of the oxyanions compared to EDTA-promoted dissolution in their absence.

Acknowledgements

I would first like to offer my most sincere gratitude to Dr. Matt Eick, who has been my major professor and advisor. I have learned a lot and most importantly, have gained a true appreciation for the science of Soil Chemistry. Matt, your enthusiasm for the subject is contagious and genuine. It has been a privilege working with you. Thank you for your assistance, insights, and patience. I would also like to thank my committee members, Dr. Zelazny and Dr. Alley, for their advice and suggestions. I would like to thank Dr. Paul Grossl for numerous C analyses and for reviewing my manuscript. I extend my gratitude to Dr. Bill Edmonds for developing my interest in Soil Science.

I would like to thank the Virginia Employment Commission (VEC) for the financial support of my education. Mrs. Mette Richards, who has been my contact there for over two years, has been so very helpful and kind.

My work on this project involved extensive laboratory experiments, and several people have been instrumental in its completion. Special thanks to Hubert Walker for the analysis of the goethite used in this study and for answering my numerous laboratory questions. I would like to thank Athena Van Lear and Nancy Phillips for ICP analysis. I am very grateful to Markus Grafe, Mindy Waltham, and Todd Luxton for not only helping me with various aspects of this project but making working on it so much more enjoyable.

I would like to thank my parents for their guidance, support, and love. Thank you from the bottom of my heart. I would also like to thank my fiancé, Larry, for his encouragement and kind words that made me want to push forward with my work. Last, but not least, I thank my friends who have made my years at Virginia Tech better than I could have ever imagined. I will truly miss you all.

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1.0 Introduction

Weathering reactions can significantly influence the development and heterogeneity of soil systems. A voluminous amount of research has been conducted examining the dissolution of primary minerals, however, much less has been conducted examining secondary mineral weathering (McBride, 1994). Secondary minerals such as oxides of iron and manganese are highly reactive and act as sinks for trace anions and cations. Dissolution of these minerals can increase micronutrient bioavailability in natural systems both through the release of adsorbed ions as well as dissolution of the mineral structure. Furthermore, in highly weathered systems Fe-oxides may be the dominant source of iron, and the dissolution and subsequent release of iron from these structures has been shown to increase in the presence of naturally occurring organic siderophores (Hersman et al., 1995). Other organic ligands (sometimes referred to as dissolved organic carbon or DOC) have also been found to influence such oxide dissolution rates (Zhang et al., 1985; Panias et al., 1996). These ligands (i.e. citrate, ascorbate, or siderophores) may be released naturally via microbial and plant physiological processes or anthropogenically. One such synthetic organic ligand, ethylenediaminetetraacetic acid (EDTA) is a complexing agent commonly used in industries and as an ingredient in household cleaning chemicals. EDTA is resistant to biodegradation and is commonly released into soil and aquatic systems via wastewater treatment effluent and less frequently via acute pollution events (Bargar et al., 1999). EDTA is often used as an analogue for DOC and previous studies have demonstrated that EDTA promotes the dissolution of naturally occurring iron oxides (Chang and Matijevic, 1983; Blesa et al., 1984;

Rueda et al., 1985; Miller et al., 1986; Borggaard, 1991; Bondietti et al., 1993; Nowack and Sigg, 1996; Ballesteros et al., 1998).

In natural systems, mineral dissolution can be influenced by the presence of inorganic oxyanions. Research has suggested that the type of surface complex formed by the oxyanion can effect the organic ligand-promoted dissolution of Fe-oxides (Stumm, 1992; Bondietti et al., 1993; Biber et al., 1994). There are several types of surface complexes, each of which is differentiated by the number of bonds a single sorbing molecule forms with one or more central ions (Figure 1). A monodentate complex consists of one bond (Figure1a), while a bidentate complex consists of two bonds to the same central ion (Figure 1b). If a sorbing molecule is bonded to only one central ion, it is referred to as a mononuclear complex. If a single molecule is bound to two or more central ions, it is a bi- or multinuclear surface complex, respectively (Figure 1c). Mononuclear complexes formed by the oxyanions are thought to enhance dissolution, while binuclear complexes inhibit dissolution (Stumm, 1992; Bondietti et al., 1993; Biber et al., 1994). Mononuclear surface complexes are weaker than multinuclear complexes because they are made up of fewer bonds that link the molecule to the oxide. It has been suggested that this makes the oxide more susceptible to dissolution compared to an oxide with multinuclear linkages that tend to enhance the strength of the structure (Stumm, 1992).
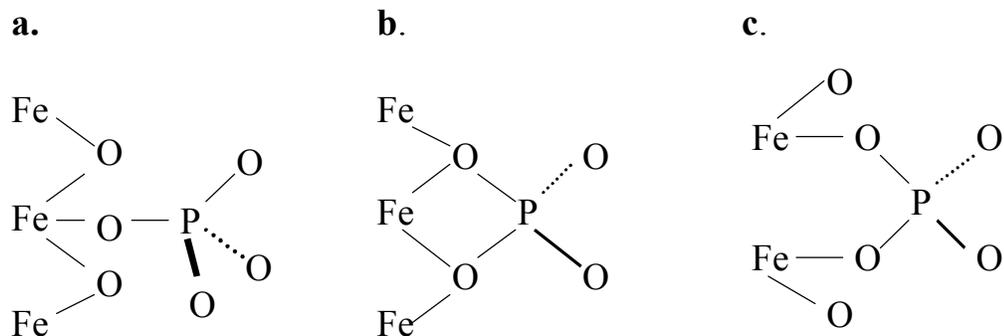
Figure 1 Surface Complexes: (a) Monodentate, (b) Bidentate, and (c) Binuclear.

However, other studies have been conducted that suggest that the oxyanions do not directly effect the dissolution of oxide minerals (Borggaard, 1991; Eick et al., 1999). For example, Eick et al. (1999) proposed that oxyanions influence organic ligand-promoted dissolution of goethite by occupying adsorption sites and reducing the amount of organic ligand adsorbed to the surface. A reduction in the adsorption of the dissolution enhancing ligand reduces the dissolution rate. Borggaard (1991) proposed that oxyanions indirectly affect the EDTA-promoted dissolution of Fe-oxides by shifting the EDTA complex from multinuclear (dissolution inhibiting) to mononuclear (dissolution enhancing).

The discrepancies in the literature surrounding the role of oxyanions in organic ligand-promoted dissolution warrants further investigation. In this study, we examine the influence of phosphate, selenite, and molybdate on the EDTA-promoted dissolution of goethite.

1.1 Adsorption of Oxyanions on Mineral Oxide Surfaces

The adsorption of oxyanions on Fe-oxide surfaces may influence the organic ligand-promoted dissolution of the oxides via several processes including competition for adsorption sites, changes in surface charge, and changes in the strength of the crystalline structure. The oxyanions chosen for this study, selenite (SeO_3^{2-}), molybdate (MoO_4^{2-}), and phosphate (PO_4^{3-}) are animal and plant micro- and macronutrients that are commonly present in soil systems. Their adsorption behavior on aluminum and iron oxides has been extensively studied, especially phosphate. Goethite is often selected as the variable charged surface for these studies because it is one of the most abundant iron (hydr)oxides found in soils worldwide (Schwertmann and Cornell, 1996). Furthermore, although it does not comprise a large percentage of the clay-sized fraction, the oxide often coats the surfaces of other mineral constituents and can significantly influence the adsorption characteristics of soil (Hendershot and Lavkulich, 1983).

Selenite, molybdate, and phosphate have been found to adsorb on goethite by a ligand exchange mechanism (Hingston et al., 1972; Parfitt, 1978; Ferreiro et al., 1985; Balistrieri and Chao, 1987; Zhang and Sparks, 1989; Parfitt, 1989; Torrent et al., 1990; Strauss et al., 1997; Papadopoulos et al., 1998). Ligand exchange is the release of H_2O and/or OH^- as the adsorbate (i.e. oxyanion) bonds to a surface Fe atom (Figure 2). The initial ligand exchange rate has been found to be rapid on external adsorption sites, with a second weaker exchange reaction following, and lastly, there is a slow diffusion of the oxyanion into the defects and micropores of the mineral oxide (Parfitt, 1989; Grossl, et al., 1997).

Adsorption edges or isotherms are graphs that represent the amount of adsorbate adsorbed on a mineral surface versus pH that are often used to describe oxyanion adsorption on iron (hydr)oxides. For example, Balistrieri and Chao (1987) found the greatest adsorption of selenite on goethite at pH values ≤ 4, which is in accordance with similar studies (Hingston et al., 1972; Saeki and Matsumoto, 1994). Reyes and Jurinak (1967) determined that the molybdate adsorption reaction is dependent on pH and the quantity of oxides present in the soil. They studied the adsorption of molybdate on hematite (Fe_2O_3) at two pH values and found that the adsorption at pH 7.75 was roughly 5 times less than at pH 4; these results are also consistent with the other research (Reisenauer et al., 1962; Reyes and Jurinak, 1967; McKensie, 1983; Zhang and Sparks, 1989; Bibak and Borggaard, 1994; Goldberg and Forster, 1998). Phosphate adsorption on iron oxides is also greatest at low pH and decreases as pH increases (Parfitt, 1978; Yekini et al., 1986; Strauss et al., 1997; Ioannou et al., 1998). The adsorption of weak acids follows this trend because the adsorption is strongest at pH values near their acid disassociation constants (Hingston et al., 1972; McBride, 1994). The pK_a values of molybdic acid, phosphoric acid, selenic acid, and EDTA are listed in Table 1 (Weast, 1986).

Table 1. Acid Disassociation Constants[+]

Acid	pK$_a$ 1	pK$_a$ 2	pK$_a$ 3	pK$_a$ 4
Molybdic	3.60	4.08	-	-
Phosphoric	2.00	6.59	12.67	-
Selenic	2.50	7.31	-	-
EDTA	2.00	2.65	6.18	10.30

[+]Values from (Weast, 1986).
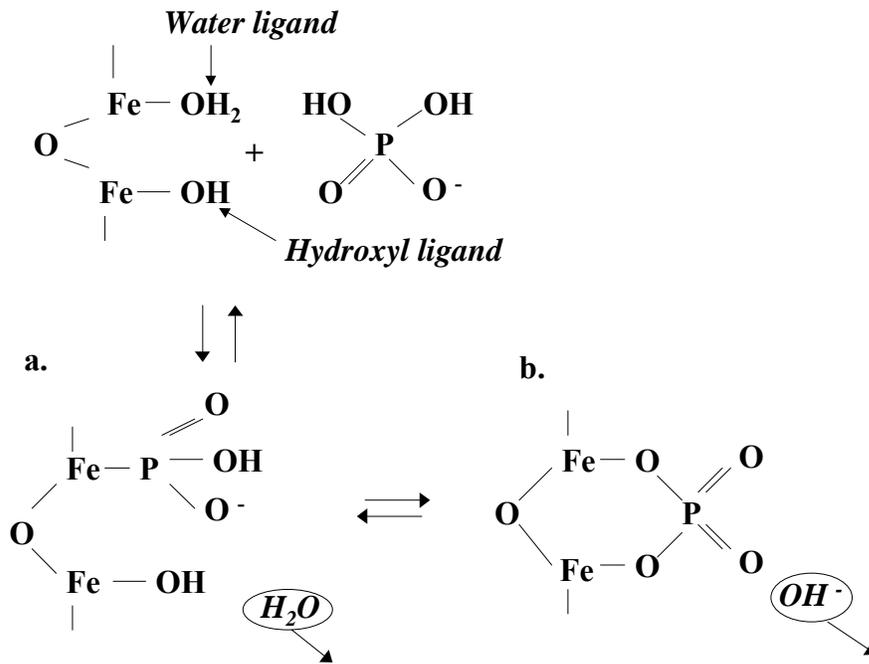
Figure 2 Schematic of ligand exchange mechanism. (a) Release of H_2O as phosphate binds and (b) release of OH^{-} as phosphate binds.

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A great deal of research has been conducted examining the mechanism of oxyanion adsorption (e.g. inner- versus outer-sphere). In general it is assumed that inner-sphere complexes will be less mobile than outer-sphere and understanding sorption mechanisms will help one to better understand the potential bioavailability of oxyanions in natural systems. Before the advent and accessibility of in-situ surface spectroscopies (e.g. X-ray absorption spectroscopy), macroscopic techniques were used to provide insight on oxyanion adsorption mechanisms. For example, surface charge properties of oxide minerals have been used extensively to examine oxyanion adsorption (Hiemstra et al., 1989; Stumm, 1992). Most Fe-oxide surfaces have point of zero charge (PZC) values around 8 (McBride, 1994). Above this pH value, the surface will be negatively charged and below this value it will be positively charged. Although strong acid oxyanion adsorption decreases as pH increases there still is significant adsorption above the PZC, which is indicative of inner-sphere adsorption or chemisorption. Additionally, chemisorption of oxyanions shifts the PZC of Fe-oxides to lower pH values. Several researchers observed this shift to lower pH values for phosphate, selenite, and molybdate (Parfitt, 1975; Rajan, 1979; McKensie, 1983). A shift in the PZC is characteristic of chemisorption. Other factors such as ionic strength have been used indirectly to determine if an oxyanion is chemisorbed to an oxide surface. Chemisorption of an oxyanion is associated with little or no ionic strength effects (McBride, 1994). Ionic strength has been found to have a minimal effect on the adsorption of selenite, molybdate, and phosphate to goethite, with adsorption slightly lower at ionic strengths as high as 1.0 M (Yekini et al., 1986; Goldberg and Forster, 1998; Su and Suarez, 2000).

Recently researchers have employed spectroscopic techniques to determine the type of surface complex formed by these oxyanions on mineral oxide surfaces. Using Extended

X-ray Adsorption Fine Structure (EXAFS) spectroscopy, Hayes et al. (1987) reported that selenite forms a strong inner-sphere binuclear complex with goethite in which the oxyanion is directly coordinated to two surface oxygens, which are bonded to two Fe atoms. Su and Suarez (2000) used Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy and determined that selenite adsorbs by multiple bonds. Other researchers also suggest that selenite binds as a binuclear and/or bidentate complex with Al and Fe oxides (Parfitt, 1978; Rajan, 1979; Tejedor-Tejedor and Anderson, 1986; Manceau and Charlet, 1994).

Phosphate adsorption has been examined using infrared spectroscopic techniques (Atkinson et al., 1973; Parfitt et al., 1975; Nanzyo and Watanabe, 1982; Tejedor-Tejedor and Anderson, 1986). Each of these studies concluded that two phosphate oxygen atoms bind to two Fe ions forming a binuclear surface complex.

Spectroscopic techniques have not been frequently used to describe molybdate adsorption; however, several studies compare molybdate adsorption to phosphate and predict a binuclear surface complex (Theng, 1971; Ferreiro et al., 1985; Bibak and Borggaard, 1994). Additionally, Zhang and Sparks (1989) conducted a kinetic study of molybdate adsorption on goethite using pressure jump relaxation and determined that it forms a strong inner-sphere complex.

The adsorption (or chemisorption) of oxyanions can have a profound effect on their potential bioavailability in natural systems. For example, selenium was first observed to be toxic to aquatic life in 1982 at the Kesterson Reservoir in the San Joaquin Valley in California (Frankenberger and Engberg, 1998). After constructing a drainage system in the Valley, several species of waterfowl that inhabited the wetland began to experience birth defects. Biologists discovered high Se levels in all of the declining waterfowl species. It was

found that naturally occurring Se was concentrated in drainage waters from agricultural practices. In this case, the high pH of the water and the presence of Se in its oxidized form (selenate) precluded chemisorption on oxide surfaces hence increasing its bioavailability.

Molybdenum can be toxic to grazing animals in excessive concentrations (Reisenauer et al., 1962). Molybdenosis is a disease that causes stunted growth and deformities in cattle that forage on plants that contain greater than 5 ppm Mo (Tisdale et al., 1993). Molybdenosis is primarily associated with calcareous soils where the high pH limits Mo adsorption and increases its bioavailability.

In recent years, there has been a national focus on eutrophication of inland bays and marshes and the role of phosphorus. Scientists have observed a decline in all types of aquatic life in natural waters, including the Chesapeake Bay, due to the overgrowth of algae spawned by eutrophication. Eutrophication is a result of excess levels of nutrients such as phosphorus reaching the Bay. The increase in nutrients causes the excessive growth of algae, which decays and dramatically reduces dissolved oxygen levels. In this case, there is some evidence that phosphorus released into water bodies may be associated with colloidal Fe-oxides (Logan, 1992). These oxides may reductively dissolve upon settling and release phosphorus into the environment. The above examples illustrate the importance of examining the adsorption of these oxyanions and their effect on the dissolution of mineral oxides, which can lead to a better understanding of the mobility and potential toxicity of these constituents in natural systems.

1.2 Adsorption of EDTA and EDTA-Promoted Dissolution of Metal Oxides
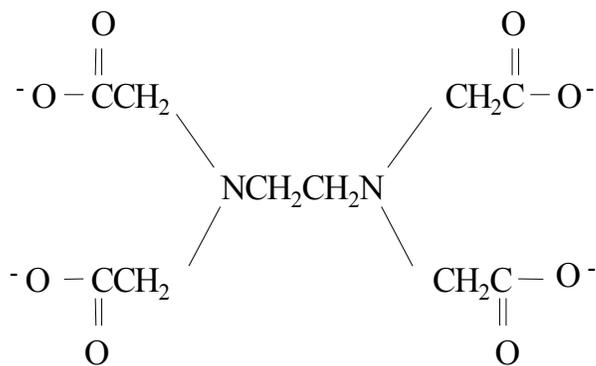
Figure 3 Structure of EDTA molecule.

Ethylenediaminetetraacetic acid (EDTA) is a complexing agent commonly used in industries and household cleaning chemicals. For example, EDTA has been used to decontaminate the components of nuclear reactors because of its ability to dissolve Fe-oxides (Litter and Blesa, 1987). Due to the low biodegradability of EDTA, it is often released into soil and aquatic systems via wastewater treatment effluent and less frequently via acute pollution events (Means et al., 1980). EDTA has a tendency to bind with divalent metal cations and form metal complexes that have adsorption behaviors similar to those of anions (Szecsody et al., 1994). EDTA is similar to other organic ligands in that it has the ability to accelerate the dissolution of oxide minerals. Researchers have examined such behavior of these metal complexes and the influence on mineral oxide dissolution (Blesa et al., 1984;

Borggaard, 1991; Bargar et al., 1999). Ballesteros et al. (1998) examined the EDTA-promoted dissolution of goethite and found that the affinity of these metal-EDTA complexes for the goethite surface sites is comparable to the affinity of uncomplexed (or free) EDTA for the same sites. Nowack and Sigg (1996) found that metal-EDTA complexes adsorb differently depending on the metal, with trivalent metal complexes being adsorbed very weakly compared to divalent metal complexes. They also found that the dissolution rate of iron (hydr)oxides is significantly reduced when EDTA is present as a metal complex compared to uncomplexed EDTA (Nowack and Sigg, 1997).

The adsorption of EDTA on the surface is the prerequisite step to the EDTA-promoted dissolution of goethite. The adsorption of EDTA on goethite has been studied by several researchers (Rueda et al., 1985; Nowack and Sigg, 1996; Bargar et al., 1999). The mechanism is considered a ligand exchange in which the ligand ($EDTA^{4-}$) adsorbs on specific sites ($\equiv$Fe-OH) on the surface and releases ligands in the form of hydroxyls and water, as follows:

$$\equiv\text{Fe-OH} + EDTA^{4-} + H^+ \rightarrow \equiv\text{Fe-}EDTA^{3-} + H_2O \qquad (1)$$
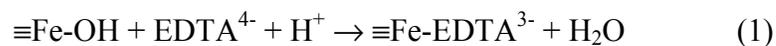
Nowack and Sigg (1996) derived this reaction by using the constant capacitance model, a standard surface complexation model that is frequently used to study adsorption characteristics.

EDTA has four carboxyl groups that may adsorb to four central Fe atoms (Borggaard, 1991) (Figure 3). Szecsody et al. (1994) suggests that each molecule of EDTA adsorbed on an oxide surface can bind to two or more sites because of its large size. EDTA molecules are so large relative to the Fe atoms of iron oxides that the adsorption reaction is slow compared to other ligands such as oxalate or citrate (Miller et al., 1986). The affinity of EDTA for an

oxide surface is heavily dependent on pH (Ballesteros et al., 1998). EDTA adsorption on iron oxides is greatest at low pH, with a maximum adsorption at approximately pH 3 or 4, and the adsorption steadily declines as pH increases (Blesa et al., 1984; Rueda et al., 1985; Bondietti et al., 1993; Nowack and Sigg, 1996). It has been proposed that at pH values < 7, EDTA forms multinuclear surface complexes with goethite, and at pH values > 7 it will form mononuclear complexes (Nowack and Sigg, 1996; Stumm, 1997). In contrast, Blesa et al. (1984) examined the adsorption of EDTA on magnetite and found that the number of adsorption sites changes from 2 to 4 as pH increases. Therefore, at low pH, they propose that EDTA adsorbs as a mononuclear surface complex and as pH increases, each molecule binds to multiple Fe atoms (Blesa et al., 1984; Rueda et al., 1985). These discrepancies necessitate further examination of EDTA adsorption on iron oxides and generate questions as to how dissolution trends differ based on the type of surface complex formed by the ligand upon adsorption.

It is generally accepted that the ligand-promoted dissolution of oxide minerals is a surface-controlled reaction occurring in steps (Stumm, 1992; Panias et al., 1996). The first step is the adsorption of the ligand on the oxide surface (as described above), most commonly by a ligand exchange mechanism. This step is very fast compared to the dissolution reaction. Upon adsorption, the surface complex weakens the metal-oxygen bonds on the surface of the crystal lattice. The ligand is covalently bonded to the structural metal and has a tendency to polarize the metal-oxygen bonds, which lowers their activation energy. Furthermore, adsorption of the ligand decreases the net surface charge of the oxide, which increases surface protonation. Both of these reactions diminish critical metal-oxygen bonds

and facilitate the dissolution of the oxide mineral. Thus, the overall dissolution rate is proportional to the rate of breaking a metal-oxygen bond (Stumm, 1997).

The EDTA-promoted dissolution of iron oxides has been examined with regard to many factors (Chang and Matijevic, 1983; Blesa et al., 1984; Rueda et al., 1985; Miller et al., 1986; Nowack and Sigg, 1997). Chang and Matijevic (1983) studied the EDTA-promoted dissolution of hematite (α-Fe_2O_3) and found that temperature and pH greatly influence the release of iron from the structure. They determined that dissolution is greater as temperature increases (> 64°C) in acidic solutions (Chang and Matijevic, 1983). Rueda et al. (1985) found the EDTA-promoted dissolution of goethite to reach a maximum at approximately pH 9 at 30°C and at pH 3 at 50°C. They suggest that the differences are related to the increasing importance of nonreductive dissolution pathways as temperature is increased (Rueda et al., 1985). Blesa et al. (1984) examined the dissolution of magnetite (Fe_3O_4) by EDTA and found the dissolution rate to be higher at low pH values. The concentration of protons at low pH values increases the activation energy, which breaks the Fe-O bonds of the mononuclear surface complex and promotes dissolution (Blesa et al., 1984). Miller et al. (1986) compared the effectiveness of thirteen organic acids to dissolve crystalline (goethite and hematite) and noncrystalline iron oxides. They found that EDTA completely dissolved the noncrystalline oxides within a few days and goethite and hematite, with smaller surface areas were more resistant and only partially dissolved. The EDTA-promoted dissolution was found to be the greatest at pH 3.5 as opposed to pH 5.5 for the majority of the organic acids (Miller et al., 1986).

Conversely, Nowack and Sigg (1997) determined that the dissolution of goethite by EDTA increases with increasing pH, with a maximum at approximately pH 8. They suggest

that this is a result of EDTA binding as a binuclear complex at low pH and a mononuclear

complex at high pH (Nowack and Sigg, 1997). Given the above discrepancies, the

mechanisms of EDTA adsorption and dissolution warrant additional examination.

1.3 The Effect of Oxyanions on the Ligand-Promoted Dissolution of Metal Oxides

Competing oxyanions, such as phosphate, selenite, and molybdate, can minimize ligand-promoted dissolution by occupying reactive surface sites and hence reducing adsorption of the ligand. Researchers have found that oxyanions such as phosphate and arsenate can effectively reduce the dissolution of iron oxides (Biber et al., 1994; Bondietti et al., 1993). Biber et al. (1994) presented data examining the influence of oxyanions on the dissolution of Fe(III) hydroxides. Phosphate, arsenate, sulfate, and borate were found to be dissolution-inhibitors, especially phosphate, which nearly prevented the dissolution of goethite. It was suggested that the dissolution rate was inhibited because the oxyanions formed binuclear surface complexes. In order for the oxide to dissolve, both center Fe atoms would be removed simultaneously, creating an energetically unfavorable process (Bondietti et al., 1993; Stumm, 1997). It has been stated that oxyanions that form mononuclear complexes with the surface are dissolution enhancing; while those forming bi- or multinuclear complexes inhibit dissolution (Stumm, 1997).

Two studies have been conducted that examine the influence of oxyanions on the EDTA-promoted dissolution of iron oxides (Borggaard, 1991; Bondietti et al., 1993). Borggaard (1991) studied the effects of phosphate on iron oxide dissolution in the presence of EDTA. The addition of phosphate was found to increase the dissolution rate of goethite at pH 5. Borggaard (1991) suggested that the increased dissolution rate may be attributed to a reduction in the number of EDTA groups bound to the iron oxide surface because of competition between the phosphate and the EDTA for adsorption sites. This changed the

EDTA conformation from multinuclear (dissolution inhibiting) to mononuclear (dissolution enhancing). Bondietti et al. (1993) investigated the effect of phosphate, arsenate, and selenite on the EDTA-promoted dissolution of lepidocrocite (γ-FeOOH) over a pH range of 3 to 11. They observed accelerated dissolution rates at pH<5 and a decrease in the dissolution at near neutral pH values. In contrast to Borggaard (1991), they attributed these differences to the type of surface complex formed by the oxyanion. It was proposed that binuclear complexes formed by the oxyanions at higher pH values inhibited dissolution while mononuclear complexes formed at low pH values enhanced dissolution.

This discrepancy was recently resolved by Eick et al. (1999) who demonstrated that the type of surface complex formed by the oxyanions was not responsible for the differences in dissolution rates. Eick et al. (1999) examined the effect of chromate and arsenate on the oxalate-promoted dissolution of goethite. They found that these oxyanions, which can form either mononuclear or binuclear surface complexes depending on surface coverages, inhibited the dissolution even when they formed mononuclear complexes. They proposed that chromate and arsenate inhibited the dissolution by limiting the number of surface sites available for oxalate, which decreases oxalate adsorption and impedes the dissolution effect of the ligand. The results indicated that the oxyanions were effective inhibitors at all pH values except pH 6, at which the negative charge generated by anion adsorption along with low proton activity increased dissolution (Eick et al., 1999).

Given the limited amount of research on the influence of oxyanions on the EDTA-promoted dissolution of goethite and the contrary explanations, this study was conducted to examine their effect over a range of pH values and oxyanion surface coverages. Accordingly, the objectives of this study are: 1) to examine the influence of naturally occurring oxyanions

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on the EDTA-promoted dissolution of goethite, and 2) based on equilibrium and kinetic investigations, support or refute the hypothesis of Borggaard that enhanced dissolution of goethite in the presence of oxyanions is due to a shift in the EDTA surface complex from multinuclear (dissolution inhibiting) to mononuclear (dissolution enhancing). This will be accomplished by examining the effects of selenite, molybdate, and phosphate on the EDTA-promoted dissolution of goethite. These oxyanions were chosen because they are naturally found in soil systems and are known to adsorb strongly to goethite.

2.0 Materials and Methods

## 2.1 Oxide Characterization

The goethite used in these experiments was synthesized based on the method described by Schwertmann and Cornell (1991) using reagent-grade $Fe(NO_3)_3$. The procedure was altered slightly by slowly adding 4 M NaOH to achieve a higher specific surface area goethite. Excess salts were removed by electrodialysis until the conductivity of the wash solution was nearly equal to that of double-deionized water. All solutions were prepared with double-deionized water and contact with glassware was avoided to prevent silica contamination. The goethite was subsequently washed with 0.01 M HNO_3 to remove any remaining amorphous Fe phases. The clean goethite was freeze-dried and analyzed by x-ray diffraction (XRD), thermal gravimetric analysis (TGA), and field emission scanning electron microscopy (FESEM), and the results were characteristic of goethite (Figures 4-6). The goethite structure is presented in Figure 7 and shows the coordinated oxygens (Figure 7a.) and the linked Fe octahedron (Figure 7b.). Ammonium oxalate in the dark to total iron (Fe_o/Fe_t) was used to determine the presence of remaining amorphous phases (Schwertmann et al., 1985). The Fe_o/Fe_t ratio was 0.23%, indicating essentially complete conversion to goethite. The specific surface area was 87 m^2g^{-1} as determined by a five-point N_2 Brunauer-Emmett-Teller (BET) gas adsorption isotherm method (Webb and Orr, 1997).
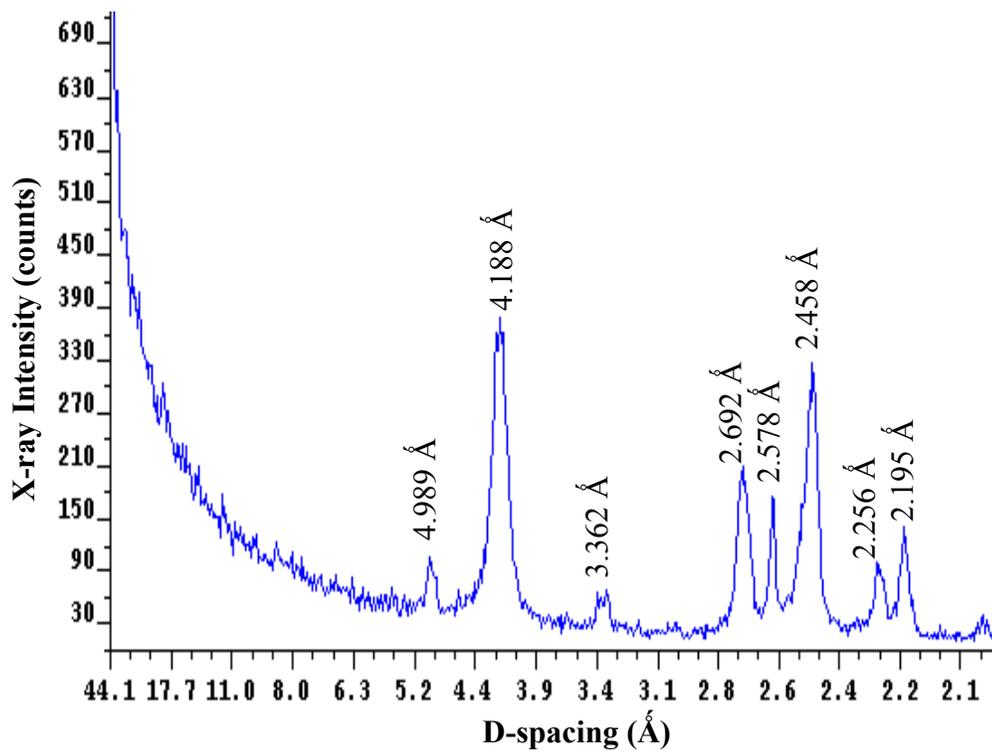
Figure 4 X-ray diffraction pattern of the goethite prepared for these experiments. The 4.18Å peak is indicative of goethite.

Sample: Goethite
Size: 28.2510 mg
Method: Hi-Res 50-1000, 20C
Comment: Jill

TGA

File: C:\TA\Data\TGA\Walker.006
Operator: H Walker
Run Date: 10-Feb-00 09:08
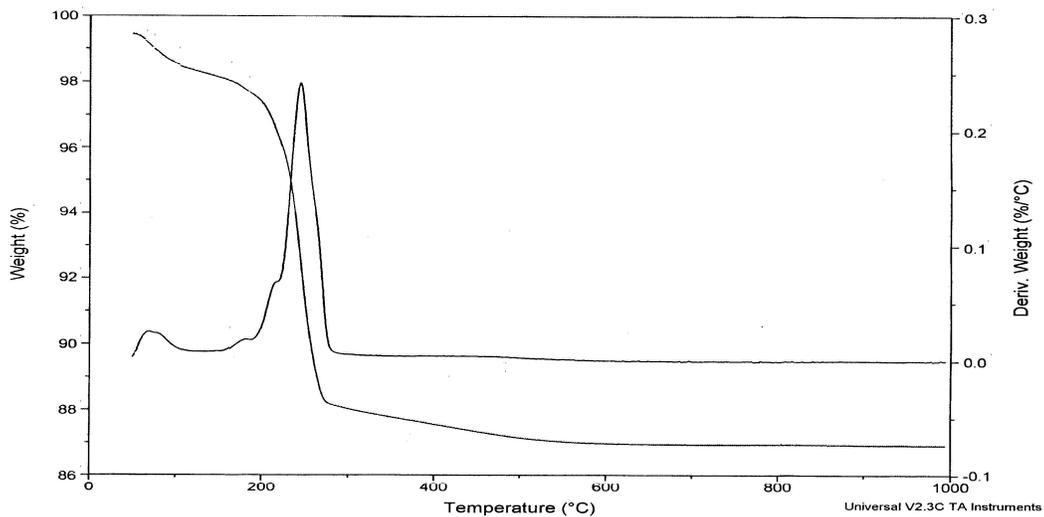
Figure 5 Thermal gravimetric analysis of the goethite prepared for these experiments.
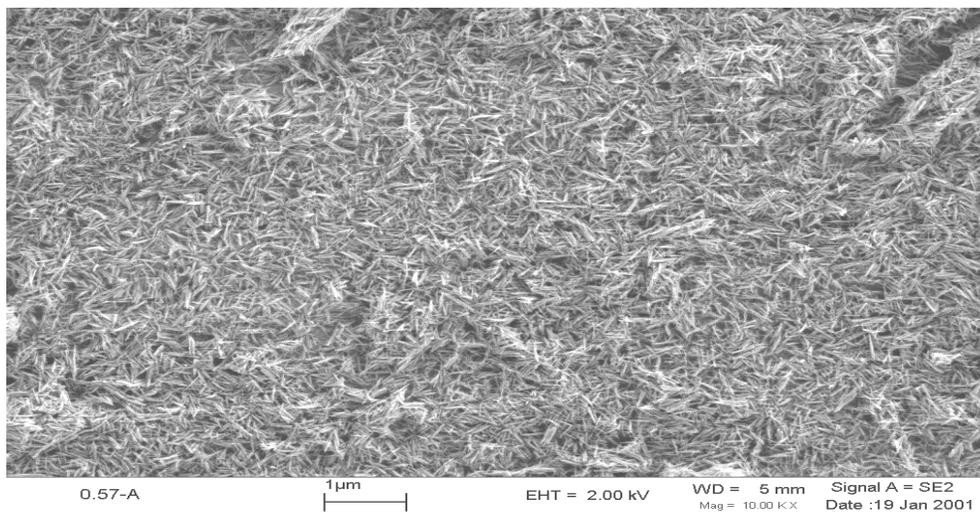
Figure 6 Scanning electron microscope image of goethite**.**
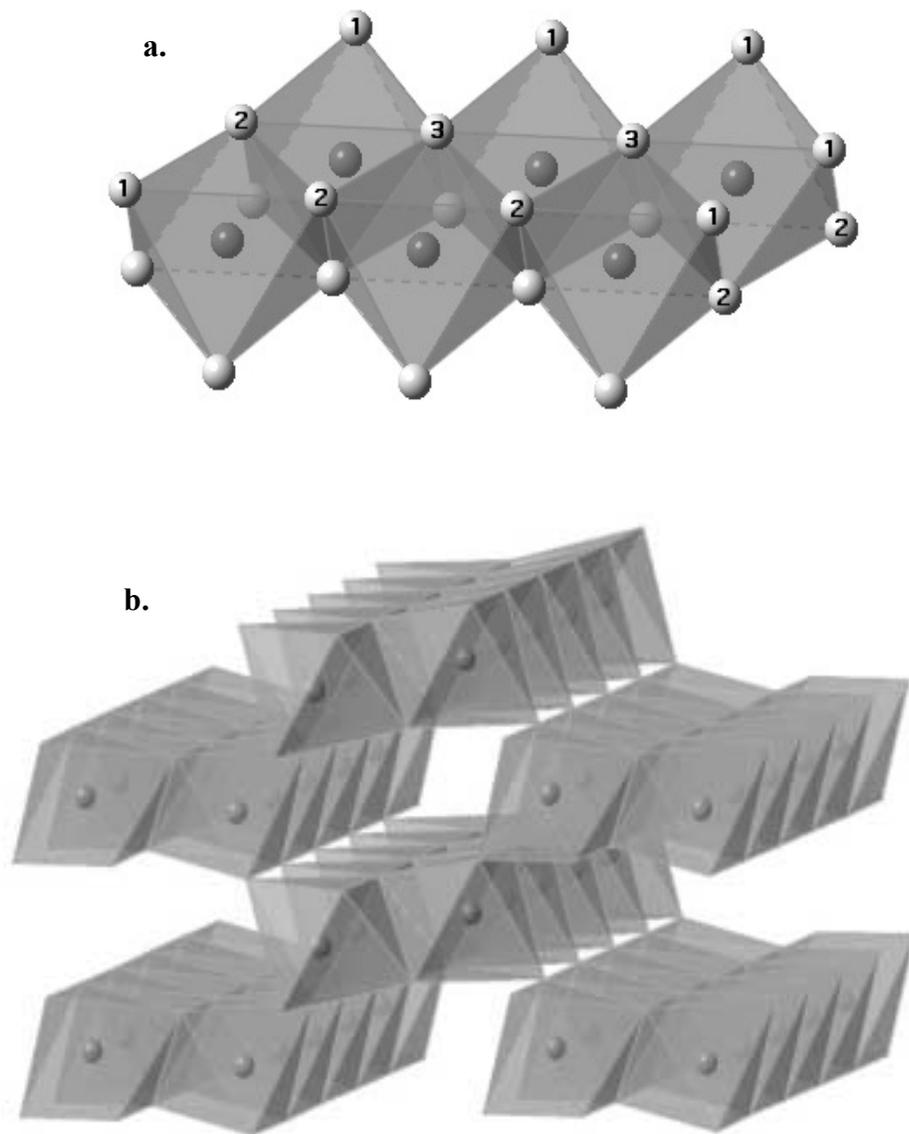
Figure 7 The structure of goethite: (a) the coordination of the oxygens is shown, with 1 representing singly coordinated, 2 representing doubly coordinated, and 3 representing triply coordinated and (b) the linked Fe octahedron.

2.2 Adsorption Edges

Figure 8 The batch reaction apparatus.

Adsorption of phosphate, molybdate, selenite, and EDTA were examined as a function of

pH (10-3) and ionic strength (0.01 and 0.001 M NaNO$_3$) at constant adsorbate (1.0 mM) and

adsorbent concentrations (2.5 gL^{-1}). Adsorption edges were conducted using a batch

technique in a flat-bottomed, teflon-lined, water-jacketed reaction vessel (500 ml) covered

with a glass lid containing ports for a stirrer, a pH electrode, N$_2$ gas, a burette tip, and a

sample pipette (Figure 8). An appropriate quantity of goethite (0.75 g) and NaNO$_3$ were

added to the batch reactor, dispersed in a sonic dismembrator, and adjusted to pH 10 using an

automatic titrator (Metrohm 718 Stat Titrino, Brinkman Instruments, Westbury, NY) and

dropwise addition of 0.10 M NaOH. The suspension was sufficiently mixed using an over-

head driven mechanical stirrer (RZR-2000, Caframo Ltd., Wiarton, ON, Canada) spinning at

approximately five revolutions per second and allowed to equilibrate for 15 h at a constant temperature of 25 ± 0.1 °C.

After approximately 15 h, an appropriate quantity of a 0.01 M stock solution of phosphate, molybdate, selenite, or EDTA (as sodium salts) was added to the suspension (total experimental suspension volume 300 ml) and allowed to equilibrate for at least 2 h. Preliminary experiments indicated that ligand adsorption was complete after this time. Approximately 6-10 ml samples were removed from the suspension and filtered through a 0.25 μm membrane (Millipore). This entire procedure was repeated at different pH values (10-3) to obtain an adsorption edge. All samples were carefully removed from the batch reactor with an electronic pipette in order to avoid changes in the total solid/solution ratio. Samples were immediately acidified using 8 M HNO$_3$. During the EDTA adsorption study, aluminum foil was thoroughly wrapped around the batch reactor to exclude light and prevent photodissolution. Phosphate, molybdate, and selenite were analyzed using a SpectroFlame FTMOA85D (Spectro Analytical Instruments, Inc., Fitchburg, MA) inductively coupled plasma atomic emission spectrometer (ICP-AES). EDTA was measured indirectly as DOC using a Phoenix 8000 Total Organic Carbon Analyzer (Tekmar, Cincinnati, OH).

2.3 Dissolution Experiments

All dissolution studies were carried out using a pH-stat technique in the presence of 1mM EDTA. An appropriate quantity (0.75 g) of freeze-dried goethite was carefully weighed into a 500-ml teflon liner and 250 ml of 0.01 M NaNO$_3$ was added. The suspension was dispersed using a sonic dismembrator and the teflon liner was placed in a jacketed reaction

vessel and allowed to hydrate for a minimum of 10 h. The suspension pH was adjusted to the appropriate value and kept constant and well stirred with the aid of an automatic titrator and a mechanical stirrer, respectively. When the pH stabilized, the suspension volume was brought to 300 ml, less the quantity of EDTA and the oxyanion to be added. The oxyanion was added (1 mM or 0.10 mM) to the suspension and allowed to equilibrate for two hours. After two hours, the EDTA (1 mM) was added to the suspension. Sampling began 1 h after the EDTA was added and continued for approximately 50 h. All samples were obtained with the same sampling procedure used for the adsorption edge experiments and all experiments were conducted in at least duplicate. Iron was analyzed using a SpectroFlame FTMOA85D ICP-AES.

3.0 Results and Discussion
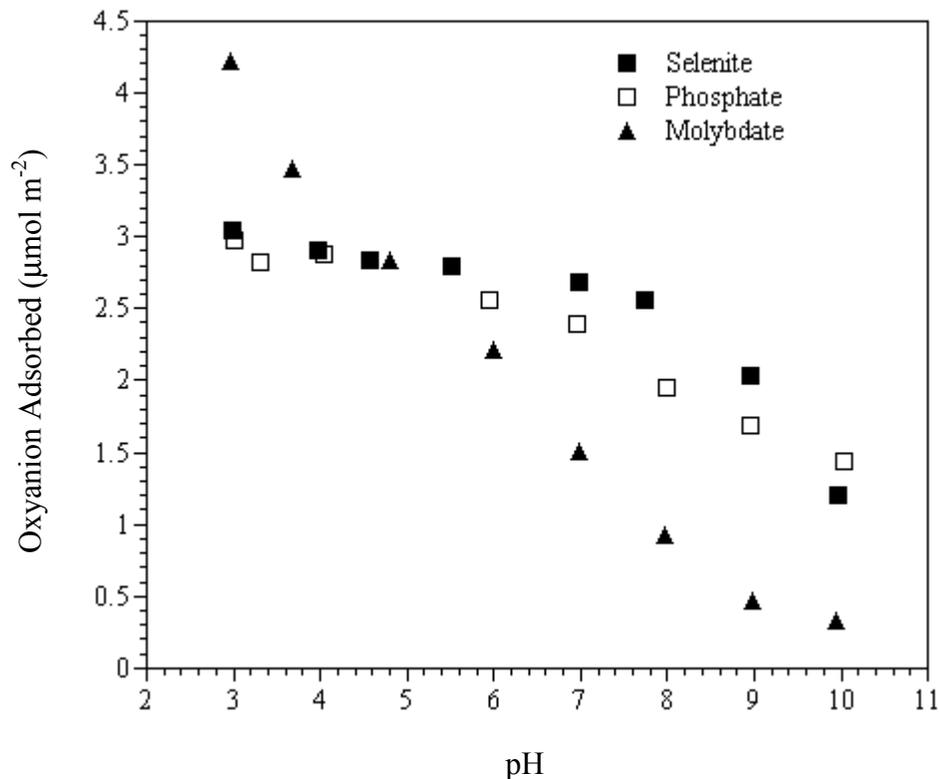
Figure 9 Adsorption edges of selenite (SeO_3^{2-}), molybdate (MoO_4^{2-}), and phosphate (PO_4^{3-}) on α-FeOOH.   α-FeOOH suspension density = 2.5 gL^{-1}, $[SeO_3^{2-}] = [MoO_4^{2-}] = [PO_4^{3-}] = 1.0$ mM, ionic strength = 0.01 M NaNO$_3$

3.1 Adsorption Edges

Phosphate, selenite, and molybdate adsorption on goethite decreased as pH increased (Figure 9). These results are consistent with other research examining oxyanion adsorption on goethite (Hingston et al., 1972; Saeki and Matsumoto, 1994; Bibak and Borggaard, 1994; Goldberg and Forster, 1998; Ioannou et al., 1998). No significant difference was observed

between the edges conducted at 0.01 M and 0.001 M NaNO$_3$, which, along with

spectroscopic and kinetic data, indicates inner-sphere adsorption (Parfitt et al., 1975;

Tejedor-Tejedor and Anderson, 1986; Zhang and Sparks, 1989; Bibak and Borggaard, 1994).

Molybdate exhibited a much steeper adsorption edge than either phosphate or selenite, which

had very similar trends. The differences in the slope of the adsorption edges between

oxyanions can be related to the degree of protonation of the molecule. In general, triprotic

acids exhibit a much broader adsorption edge over a wide pH range compared to diprotic

acids. This is because the adsorption of weak acids is strongest at pH values near their acid

disassociation constants (Hingston et al., 1972; McBride, 1994). The pK$_a$ values for these

acids are listed in Table 1.

Similar to the oxyanions, EDTA adsorbed most strongly at lower pH values (Figure 10),

which corresponds to its pK$_a$1 value of 2.0 (Weast, 1986). This trend was consistent with

other studies examining EDTA adsorption on Fe-oxides (Rueda et al., 1985; Bondietti et al.,

1993; Nowack and Sigg, 1996). The magnitude of EDTA adsorption was approximately two

orders less than that of the oxyanions because of the significantly larger size of the EDTA

molecule and its steric hindrance (Borggaard, 1991). The EDTA molecule consists of 10

carbons, with four carboxylate functional groups (Figure 3). Although EDTA can form

multinuclear surface complexes on Fe-oxides, the steric adaptation of this molecule to Fe-

oxide surface sites is slow compared to other ligands such as oxalate, resulting in

significantly less adsorption (Borggaard, 1991).
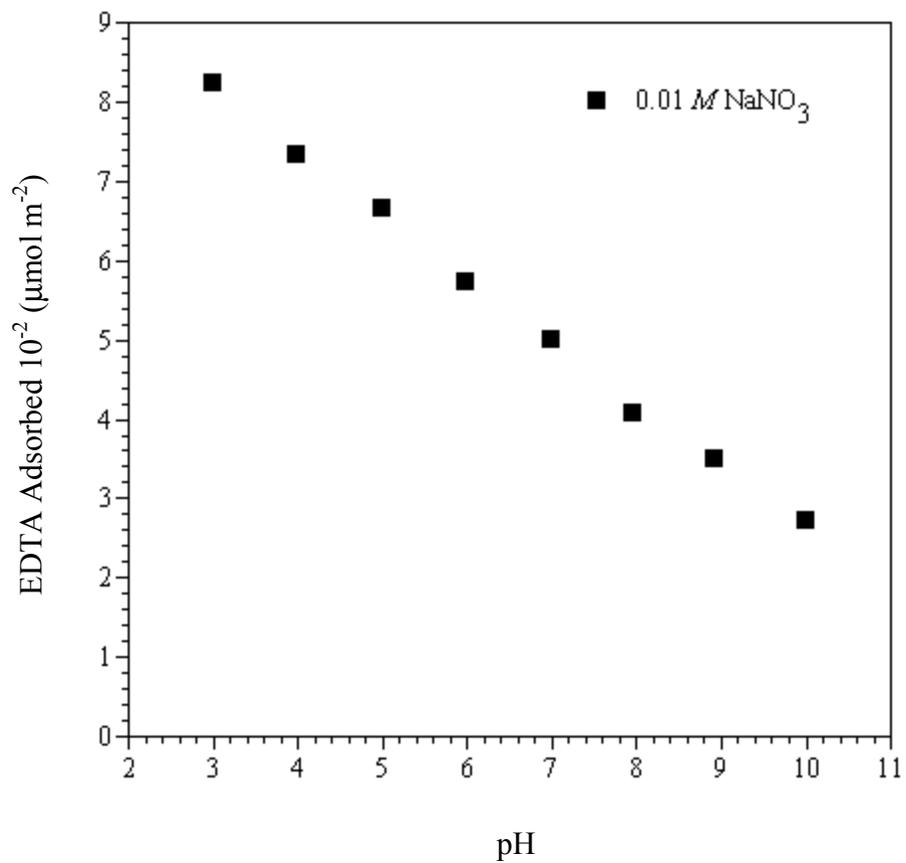
Figure 10 Adsorption edge of EDTA on α-FeOOH. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 mM, ionic strength = 0.01 M NaNO$_3$

3.2 Dissolution Studies

3.2.1 EDTA alone

Goethite dissolution rates are calculated where the rate of Fe release from the goethite structure is approximately linear and constant (>10 h) (Figure 11; Table 2). Initial dissolution rates may be controlled by the dissolution of ultra-fine particles (created during goethite synthesis) or high-energy sites caused by crystal defects and are therefore not representative of bulk dissolution rates (Casey and Ludwig, 1995). Goethite dissolution rates were greatest at pH values 4 and 5. Dissolution rates were approximately four times slower at pH values ≥ 6. Other researchers have also observed strong pH dependent dissolution rates, although their trends varied with pH (Chang and Matijevic, 1983; Bondietti et al., 1993; Nowack and Sigg, 1997). We suggest that these observed trends are associated with the type of surface complex formed by the EDTA molecule, with mononuclear complexes being dissolution enhancing and multinuclear complexes being associated with slower dissolution rates.
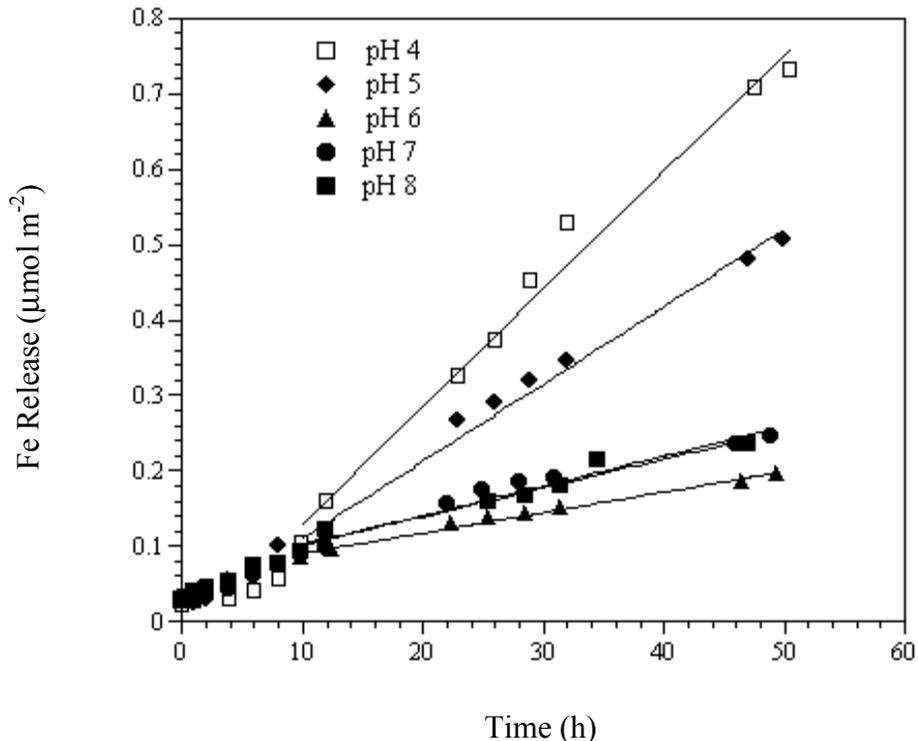
Figure 11 Fe release at different pH values over time in the presence of EDTA. α-FeOOH suspension density $= 2.5$ gL^{-1}, [EDTA] $= 1.0$ mM, ionic strength $= 0.01$ M NaNO$_3$

Bondietti et al. (1993) found a similar trend for the EDTA-promoted dissolution of lepidocrocite (γ-FeOOH). The rate determined at pH 3 (30.8 x 10^{-2} μmol m^{-2}h^{-1}) was nearly double the rate found at pH 7 (15.4 x 10^{-2} μmol m^{-2}h^{-1}). These results are contrary to those determined by Nowack and Sigg (1997), who found a maximum rate of EDTA-promoted dissolution of goethite at pH 8. They observed a nearly constant rate from pH 3-7 (approximately 3.0 x 10^{-3} μmol m^{-2}h^{-1}) and then a maximum rate at pH 8 (approximately 8.2 x 10^{-3} μmol m^{-2}h^{-1}). Chang and Matijevic (1983) found an increased rate of the EDTA-promoted dissolution of hematite (α-Fe$_2$O$_3$) at pH 7.4 (41.7 x 10^{-3} μmol m^{-2}h^{-1}) as opposed to pH 3 (6.0 x 10^{-3} μmol m^{-2}h^{-1}). We determined a maximum dissolution rate at pH 4 of 15.8 x 10^{-3} μmol m^{-2}h^{-1}, and a minimum rate at pH 6 of 2.7 x 10^{-3} μmol m^{-2}h^{-1} (Table 2.). These

observed differences in dissolution rates as a function of pH may be due to numerous factors including differences in experimental methods, pre-treatment of Fe-oxide surfaces, differences in specific surface area of the Fe-oxide, varying EDTA concentrations, the presence of light and ferrous iron promoting reductive dissolution pathways, and the presence of amorphous phases in the oxides synthesized for the studies. These differences illustrate the difficulty of predicting dissolution rates in natural systems based solely on laboratory data.

Table 2   Dissolution rates for the EDTA-promoted dissolution of goethite (2.5 gL^{-1}, 0.01 M NaNO$_3$, 1.0 mM EDTA).

Oxyanion or ligand concentration mM	pH of the solution	Dissolution rate (R_{EDTA}) μmol m^{-2} h^{-1} x 10^{-3}
EDTA only	4	15.8
EDTA only	5	10.3
EDTA only	6	2.7
EDTA only	7	3.9
EDTA only	8	3.8
1 mM Phosphate	4	1.8
1 mM Phosphate	5	2.2
1 mM Phosphate	6	1.9
1 mM Phosphate	7	2
1 mM Phosphate	8	0.3
1 mM Selenite	4	2
1 mM Selenite	5	1.5
1 mM Selenite	6	0.7
1 mM Selenite	7	0.9
1 mM Selenite	8	0.3
1 mM Molybdate	4	0.9
1 mM Molybdate	5	0.6
1 mM Molybdate	6	0.7
1 mM Molybdate	7	0.4
1 mM Molybdate	8	0.7
0.1 mM Phosphate	4	6.1
0.1 mM Phosphate	5	5.6
0.1 mM Phosphate	6	4.6
0.1 mM Phosphate	7	5.1
0.1 mM Phosphate	8	5.4
0.1 mM Selenite	4	4.7
0.1 mM Selenite	6	4.3
0.1 mM Molybdate	4	3.7
0.1 mM Molybdate	6	4.8

3.2.2 EDTA with Oxyanions
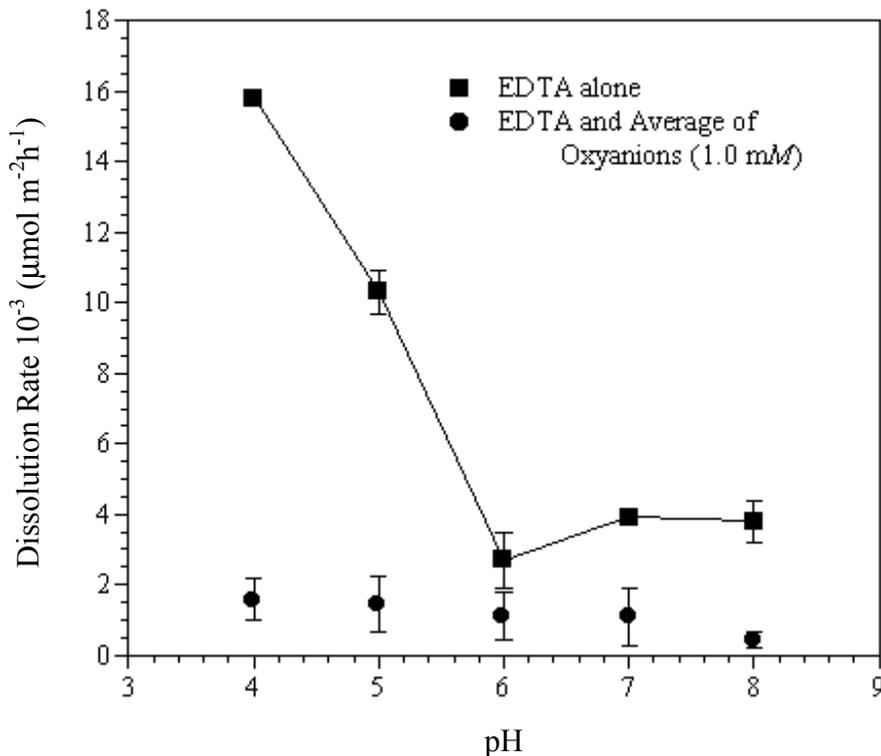
Figure 12 Comparison of goethite dissolution rates in the presence of EDTA and with the oxyanions. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 mM, [Oxyanions] = 1.0 mM, ionic strength = 0.01 M NaNO$_3$

The addition of 1 mM of phosphate, molybdate, and selenite inhibited the EDTA-promoted dissolution of goethite at all pH values (Figure 12). The error bars in Figure 12 represent the range of the values if the experiment was run in duplicate, and it represents the standard deviation of those studies run in triplicate. Based on the number of reactive functional groups available (5.5 μmol sites m^{-2}) for oxyanion adsorption on goethite and the

assumption that bidentate surface complexes predominate for the oxyanions, there would be

relatively few sites remaining on the goethite for EDTA to adsorb and hence promote

dissolution (Parfitt, 1978; Hiemstra et al., 1989). This is supported by analytical data that

shows almost no EDTA adsorption in the presence of the oxyanions at 1 m*M* (Figure 13).

This reduction in EDTA adsorption in the presence of the oxyanions results in a decrease in

the dissolution rate. Furthermore, specific adsorption of oxyanions shifts the point of zero

charge (PZC) of the goethite to lower pH values further reducing EDTA adsorption (Nanzyo

and Watanabe, 1982; McKensie, 1983; Saeki and Matsumoto, 1994; Eick et al., 1999).
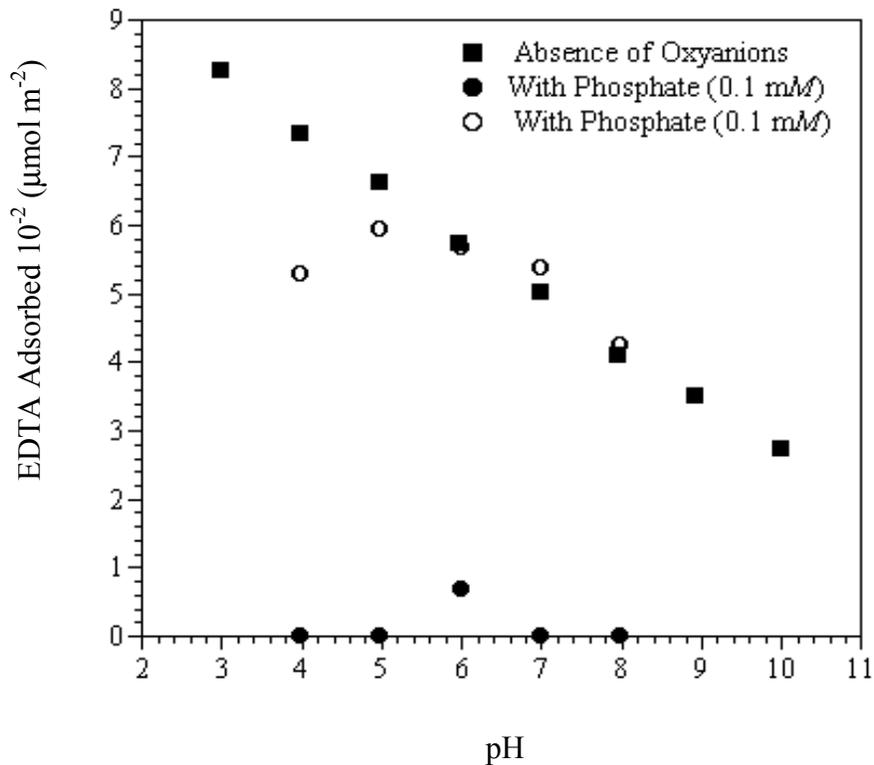

Figure 13 Comparison of EDTA adsorption in the absence and in the presence of
phosphate. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 m*M*, [Phosphate]
= 1.0 m*M* and 0.1 m*M,* ionic strength = 0.01 *M* NaNO$_3$

A second set of dissolution studies was conducted with the oxyanions at a concentration of 0.10 mM, while maintaining the EDTA concentration at 1.0 mM. Because selenite and molybdate behaved in much the same way as phosphate in terms of inhibiting EDTA adsorption (Figure 12), the influence of these oxyanions was examined at just two pH values, 4 and 6. We propose at pH values 4 and 5, in the absence of oxyanions, that EDTA adsorbs as a mononuclear surface complex and hence promotes the dissolution of goethite. When the oxyanions were present at a concentration of 1.0 mM at these same pH values, EDTA adsorption was inhibited, and dissolution rates were significantly reduced. When the oxyanion concentrations were reduced to 0.1 mM, goethite surface sites were available for EDTA adsorption and the dissolution rate increased compared to dissolution in the presence of the oxyanions at 1 mM (Figure 14). Fe release by EDTA alone and in the presence of the oxyanions at both concentrations at pH values 4 and 5 is presented in Figures 15 and 16. Assuming that EDTA forms a mononuclear (dissolution enhancing) surface complex at pH values of 4 and 5, one would expect that dissolution rates would decrease as EDTA adsorption decreases.
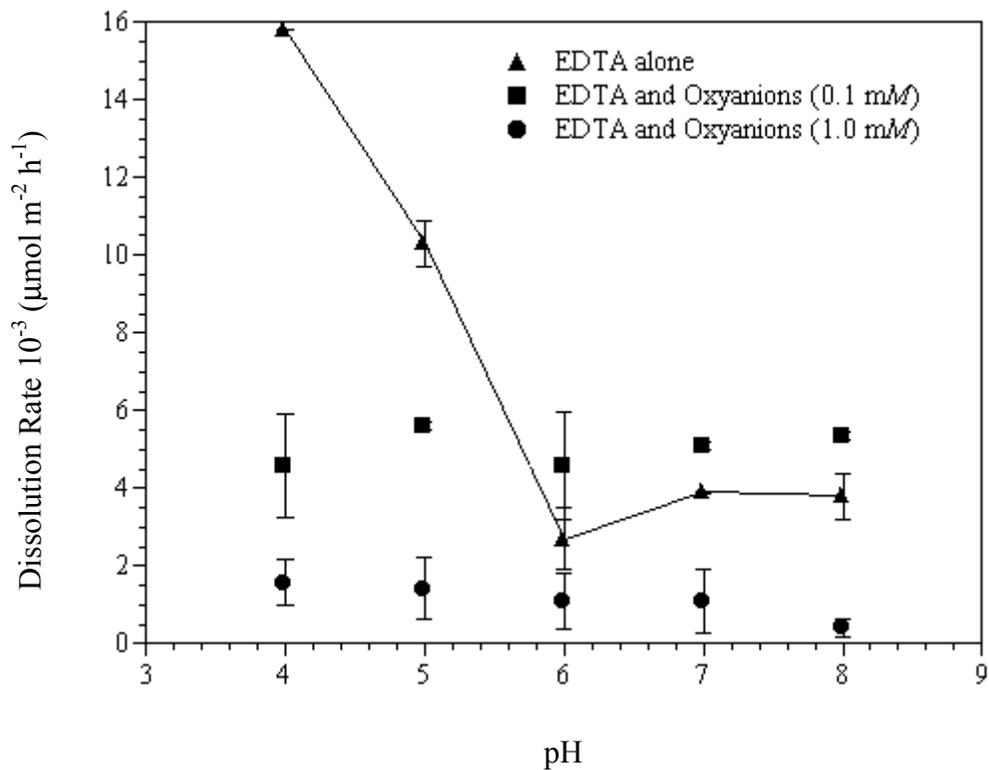
Figure 14 Comparison of the dissolution rates in the presence of EDTA and EDTA with the oxyanions at 1.0 and 0.10 mM. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 mM, [Oxyanions] = 1.0 mM or 0.10 mM, ionic strength = 0.01 M NaNO$_3$
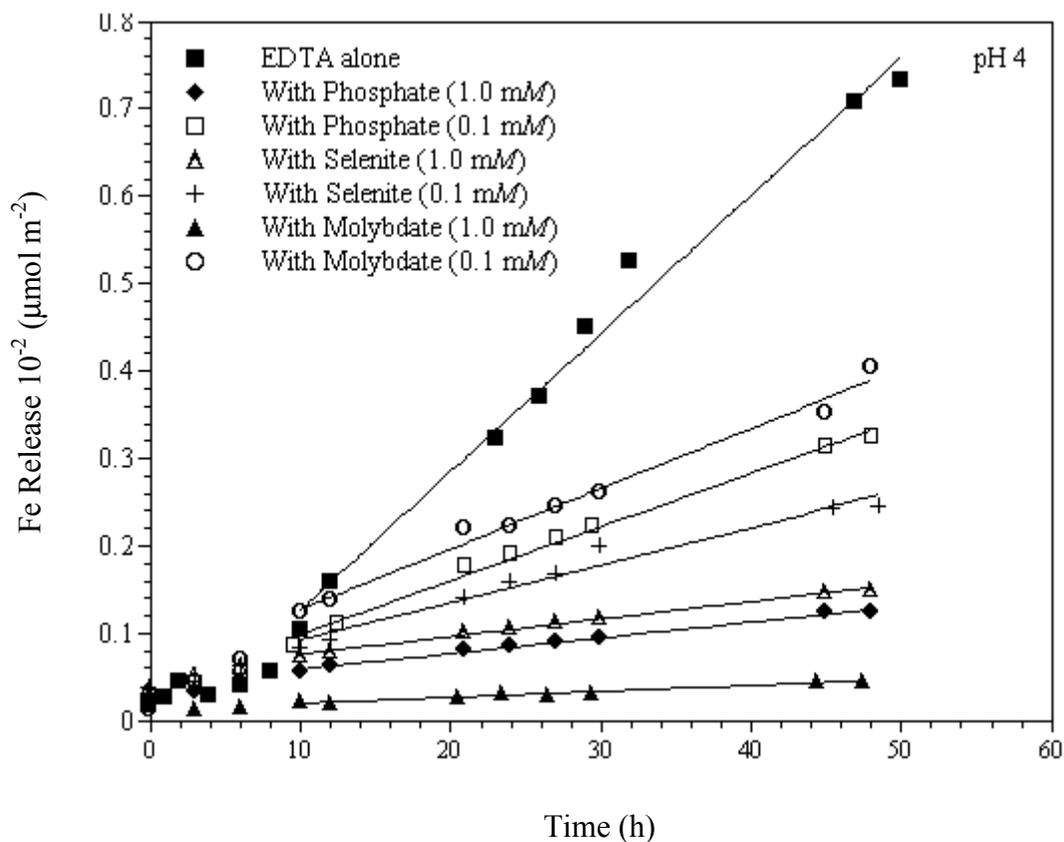
Figure 15 Comparison of Fe release from goethite at pH 4 in the presence of EDTA and EDTA with the oxyanions at 1.0 and 0.10 m*M*. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 m*M*, [Oxyanions] = 1.0 m*M* or 0.10 m*M*, ionic strength = 0.01 *M* NaNO$_3$
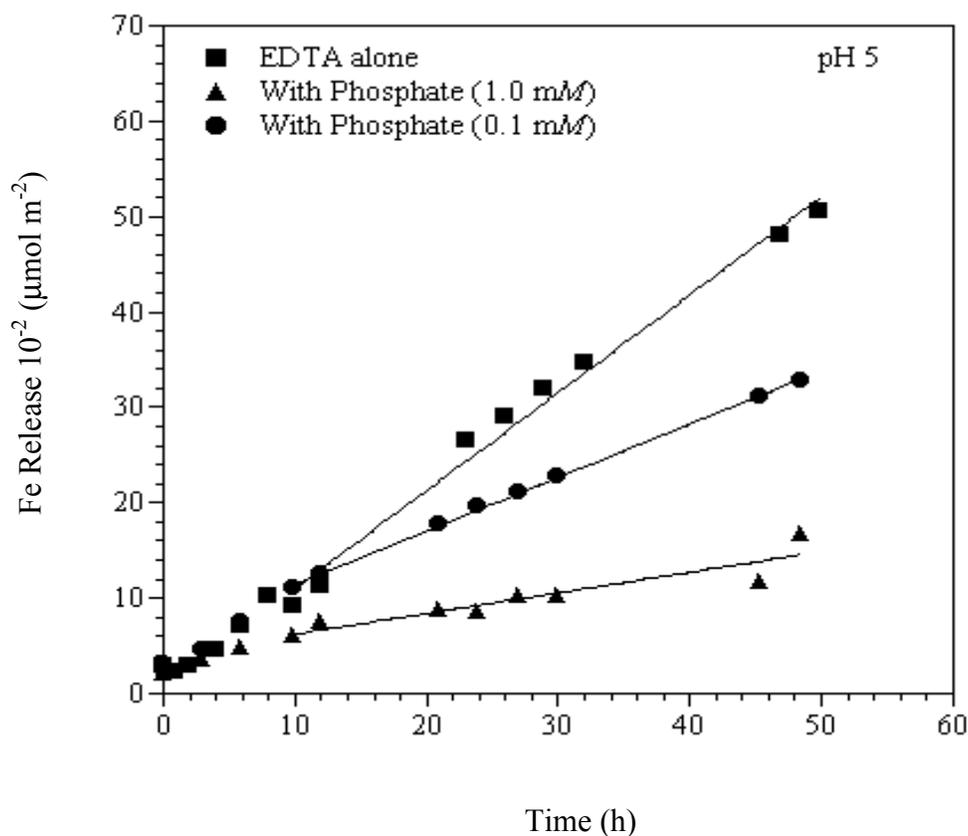
Figure 16 Comparison of Fe release from goethite at pH 5 in the presence of EDTA and EDTA with the phosphate at 1.0 and 0.10 mM. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 mM, [Phosphate] = 1.0 mM or 0.10 mM, ionic strength = 0.01 M NaNO$_3$

In the absence of oxyanions at pH values ≥ 6, EDTA adsorbed as a multinuclear complex that inhibited the dissolution rate. The Fe released by EDTA in the presence of the oxyanions at both concentrations at pH values 6, 7, and 8 is displayed in Figures 17-19. In the presence of oxyanions at 1.0 mM, EDTA adsorption was reduced and the dissolution rate decreased further. However, when the oxyanions were present at a concentration of 0.1 mM, the EDTA-promoted dissolution rate increased beyond that of EDTA alone for pH values ≥ 6 (Figure 14). By reducing the number of reactive functional groups occupied by the oxyanions, EDTA adsorption became comparable to EDTA adsorption in the absence of the

oxyanions at pH values ≥ 6 (Figure 13). We propose that the adsorption of the oxyanions

causes a reduction in the number of surface sites available for EDTA adsorption. In order for

the same amount of EDTA to adsorb in the presence of 0.1 mM oxyanions, the EDTA shifts

conformation from a multinuclear (dissolution inhibiting) complex to a mononuclear

(dissolution enhancing) complex. Mononuclear surface complexes consist of fewer bonds

and are weak compared to multinuclear surface complexes, and therefore, the bonds are more

easily ruptured which increases the dissolution rate of the goethite structure.
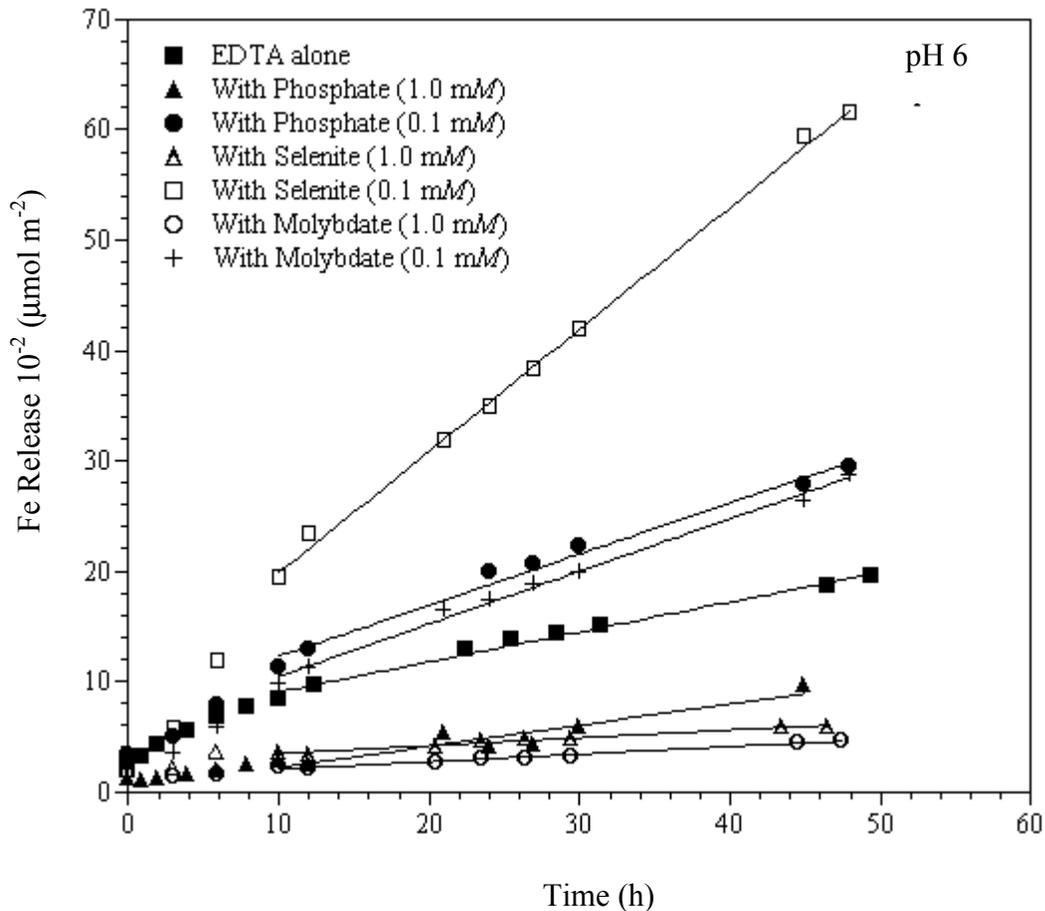
Figure 17 Comparison of Fe release from goethite at pH 6 in the presence of EDTA and EDTA with the oxyanions at 1.0 and 0.10 mM. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 mM, [Oxyanions] = 1.0 mM or 0.10 mM, ionic strength = 0.01 M NaNO$_3$
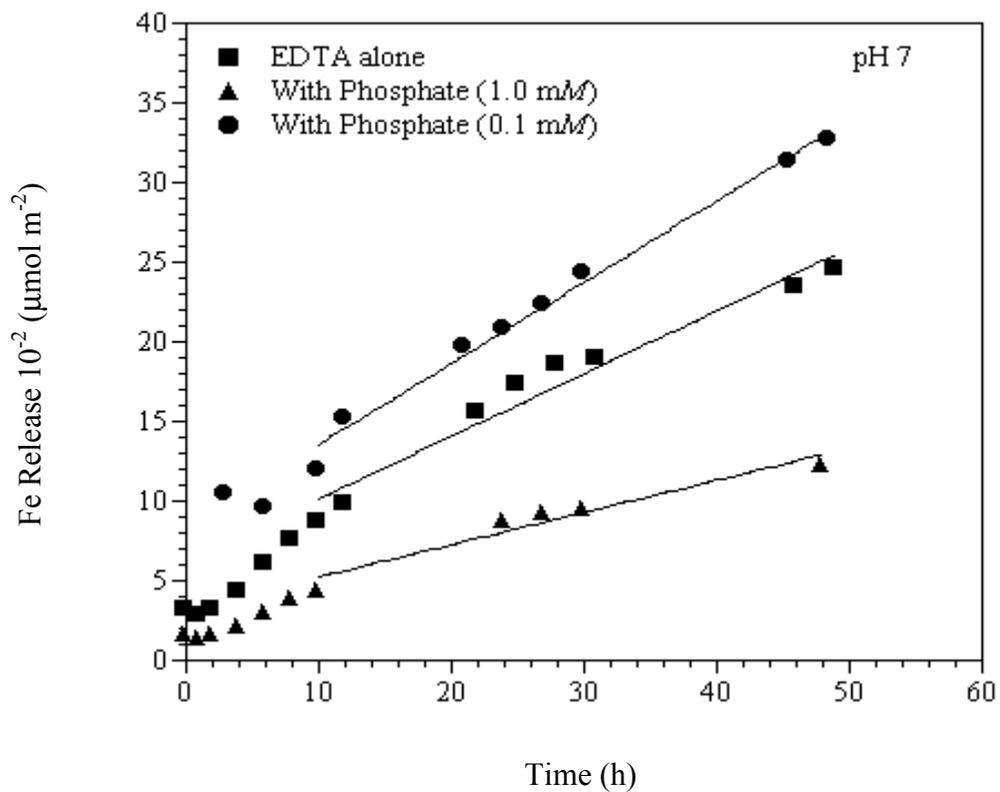
Figure 18 Comparison of Fe release from goethite at pH 7 in the presence of EDTA and EDTA with phosphate at 1.0 and 0.10 mM. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 mM, [Phosphate] = 1.0 mM or 0.10 mM, ionic strength = 0.01 M NaNO$_3$
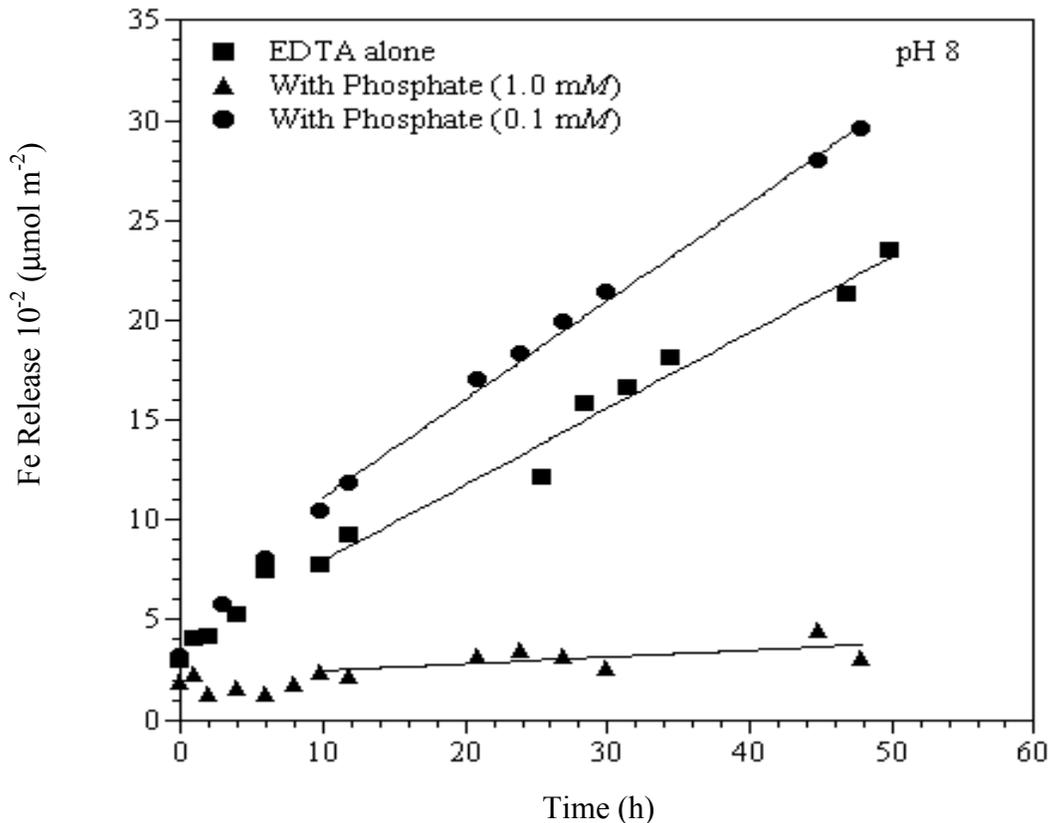
Figure 19 Comparison of Fe release from goethite at pH 8 in the presence of EDTA and EDTA with phosphate at 1.0 and 0.10 mM. α-FeOOH suspension density = 2.5 gL^{-1}, [EDTA] = 1.0 mM, [Phosphate] = 1.0 mM or 0.10 mM, ionic strength = 0.01 M NaNO$_3$

The adsorption data for the oxyanions at pH 6 at both concentrations supports the idea that by occupying surface sites the oxyanions indirectly shift the surface complex formed by EDTA. At 1.0 mM, the oxyanions occupied approximately 5.0 μmol sites m^{-2} of the total goethite surface sites available for oxyanion adsorption (5.5 μmol sites m^{-2}) (Hiemstra et al., 1989). This value was obtained by multiplying the quantity of oxyanions adsorbed by two because at these surface coverages, the oxyanions predominantly form bidentate surface complexes (Figure 14) (Parfitt, 1978; Nanzyo and Watanabe, 1982; Manceau and Charlet,

1994; Eick et al., 1999). EDTA adsorption was inhibited due to a lack of available surface sites. When the concentration of the oxyanions was decreased to 0.1 mM, they occupied 0.5 μmol sites m^{-2}, which would be 1.0 μmol sites m^{-2} assuming bidentate surface coverage. This accounts for about 1/5 of the total available sites, which shifts EDTA adsorption to a mononuclear (dissolution enhancing) conformation. Bondietti et al. (1993) also found that decreasing the concentration of the oxyanion promoted the dissolution of lepidocrocite. In this study, at pH 7 with EDTA and phosphate at equivalent concentrations, the dissolution rate was 46.2 x 10^{-3} μmol m^{-2}h^{-1}. As the phosphate concentration was decreased by one order of magnitude, the rate increased to 76.9 x 10^{-3} μmol m^{-2}h^{-1}. The above results are consistent with the results of Borggaard (1991) and Eick et al. (1999) demonstrating that dissolution of oxide surfaces is not directly affected by the type of surface complex formed but rather by the number of sites occupied by the oxyanions. However depending upon surface coverage, the oxyanions may indirectly alter the type of surface complex formed by the organic ligand hence inhibiting or enhancing dissolution relative to the organic ligand alone.

4.0 Conclusions

The influence of phosphate, selenite, and molybdate on the EDTA-promoted dissolution of goethite was examined by conducting adsorption edges for each of the oxyanions and EDTA and two sets of dissolution studies. The effect of the oxyanions at two concentrations was examined. We found that the EDTA-promoted dissolution of goethite is greater at pH values 4 and 5 than at higher pH values at both concentrations of the oxyanions. We propose that the type of surface complex formed by the oxyanions was not responsible for the changes in dissolution rates. However, by competing for the same adsorption sites, the oxyanions can indirectly influence dissolution by affecting the type of EDTA surface complex formed on the oxide surface. At pH values where EDTA forms a mononuclear (dissolution enhancing) surface complex adsorption of oxyanions reduces EDTA adsorption, which in turn reduces the dissolution rate compared to EDTA alone. At pH values where EDTA forms a multinuclear (dissolution inhibiting) surface complex, adsorption of oxyanions below monolayer surface coverages indirectly alters the type of surface complex formed by the EDTA creating a mononuclear (dissolution enhancing) surface complex. Consequently the dissolution rate is increased relative to the dissolution rate in the presence of EDTA alone. This research furthers our understanding of Fe-oxide weathering processes and Fe cycling in natural systems. This may be especially meaningful in natural systems where plants and microbes secrete siderophores, which are known to increase dissolution of Fe-oxide minerals and thus enhance iron availability.

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6.0 Vita

I am the only child of Mr. and Mrs. Emory Campbell, and I was born on November 24, 1976. I grew up in Virginia Beach and graduated from First Colonial High School in 1994. I was accepted to Virginia Polytechnic Institute and State University and eagerly anticipated entering the College of Engineering. It took me a mere semester to realize that my heart actually lied on the other side of the Drillfield. I graduated with a B.S. in Environmental Science in 1998. From there, I went to work for an environmental consulting firm. One thing was confirmed from that experience – die-hard Hokies have a difficult time living in Charlottesville.

Late in 1998, I moved back to Blacksburg and began working in the Environmental Compliance group at the Ammunitions Plant in Radford. It was a wonderful learning experience that was cut short by a reduction-in-force. It was a blessing in disguise. I had been working on a remediation project with the Army and other contractors. A particular issue came up in which several of the scientists I was working with had made an assumption about the migration of the contaminants on the project site. Something about their assumption never sat well with me. At that exact point, I became interested in Environmental Soil Chemistry.

I began my Master's program with Matt Eick in the Fall of 1999. I feel very fortunate that things have turned out the way they have. I now know why that assumption made back at the Ammunitions Plant was incorrect. I look forward to working again in site remediation with Golder Associates Inc., an environmental consulting firm in Jacksonville, FL.