

EFFECTS OF OXYANIONS ON THE EDTA-PROMOTED DISSOLUTION OF GOETHITE

JILLIAN L. CAMPBELL AND MATTHEW J. EICK*

Department of Crop and Soil Environmental Sciences, 236 Smyth Hall, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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, either enhancing or inhibiting dissolution, depending upon pH. The influence of selenite, molybdate and phosphate on the EDTA-promoted dissolution of goethite has been examined and a mechanism proposed 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 complexes accelerating dissolution compared to bi- or multinuclear complexes. Dissolution results from our experiments suggest that EDTA forms multinuclear complexes at pH values ≥ 6 and mononuclear complexes at pH values < 6 . Dissolution results show that when the oxyanion and the EDTA are present in the system at concentrations nearly equalling the surface sites available for adsorption, the oxyanion reduces the adsorption of EDTA and inhibits dissolution. However, if the oxyanion is present at lower concentrations at pH values ≥ 6 , EDTA is adsorbed but the number of carboxylic groups that can bind to the surface is reduced causing the formation of mononuclear complexes. This shift to a weaker surface complex enhances the EDTA-promoted dissolution of goethite in the presence of the oxyanions compared to EDTA-promoted dissolution in their absence.

Key Words—Adsorption, EDTA, Goethite, Kinetics, Molybdate, Oxyanions Dissolution, Phosphate, Selenite

INTRODUCTION

The dissolution of oxide minerals is an important chemical process that influences the cycling of metals, nutrients and contaminants in natural systems (Stumm, 1997). Oxide minerals are common soil components, the dissolution of which may be influenced by naturally-occurring and anthropogenic organic and inorganic ligands. One such organic ligand, ethylenediaminetetraacetic acid (EDTA), is a complexing agent commonly used in industrial 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). Previous studies have demonstrated that EDTA promotes the dissolution of naturally-occurring Fe oxides (Borggaard, 1991; Bondiotti *et al.*, 1993; Nowack and Sigg, 1997).

There are two hypotheses as to how EDTA complexes with Fe oxide surfaces. It has been postulated that at low pH, EDTA forms a bi- or multinuclear surface complex with goethite and at higher pH values, it will form a mononuclear complex (Nowack and Sigg, 1996; Stumm, 1997). These researchers observed a maximum in the

EDTA-promoted dissolution of goethite at high pH, and they attributed this to the formation of dissolution-enhancing mononuclear surface complexes. It was proposed that binuclear, or in the case of EDTA, multinuclear surface complexes, inhibit dissolution because significantly more energy is required to break two or more Fe centers from the crystalline structure (Stumm, 1992). However, Rueda *et al.* (1985) suggested a different mechanism. They conducted adsorption isotherm experiments and calculated the area of the goethite surface covered by each EDTA molecule at pH = 8 and pH = 3. The area at pH = 8 was found to be $0.93 \text{ nm}^2 \text{ molecule}^{-1}$ and at pH = 3 it decreased to $0.57 \text{ nm}^2 \text{ molecule}^{-1}$ (Rueda *et al.*, 1985). These results indicate that at higher pH values, EDTA will bind to goethite via a greater number of carboxyl groups in a multinuclear fashion and at lower pH values, fewer functional groups will be bound to the surface. This was supported by dissolution studies which found the greatest degree of EDTA-promoted dissolution at pH = 3. Discrepancies such as these are common in the literature and may be linked to experimental factors such as pH, temperature, type of Fe oxide, surface area, concentration of EDTA in solution, suspension density, and the presence of CO_2 and other competing anions.

Oxyanions such as phosphate have been found to enhance or inhibit the EDTA-promoted dissolution of mineral oxides by competing with the ligands for reactive surface sites (Borggaard, 1991; Bondiotti *et al.*, 1993). Phosphate was found to increase the

* E-mail address of corresponding author: eick@vt.edu

dissolution rate of goethite at pH 5 in the presence of EDTA. Borggaard (1991) suggested that the increased dissolution rate may have been due to a reduction in the number of EDTA groups bound to the Fe oxide surface because of competition between the phosphate and the EDTA for adsorption sites. Thus, the quantity of phosphate adsorbed changed the EDTA conformation from multinuclear (dissolution inhibiting) to mononuclear (dissolution enhancing). In contrast, Bondietti *et al.* (1993) attributed differences in the EDTA-promoted dissolution of lepidocrocite (γ -FeOOH), in the presence of several oxyanions, to the type of surface complex formed by the oxyanion, with mononuclear complexes being dissolution enhancing, and bi- or multinuclear being dissolution inhibiting.

Accordingly, the objectives of this study are: (1) to examine the influence of naturally-occurring oxyanions on the EDTA-promoted dissolution of goethite; and (2) based on equilibrium and kinetic investigations, to support or refute the hypothesis of Borggaard (1991) that enhanced dissolution of goethite in the presence of oxyanions is due to a change in the EDTA surface complex from multinuclear (dissolution inhibiting) to mononuclear (dissolution enhancing).

MATERIALS AND METHODS

Oxide characterization

The goethite used in these experiments was synthesized based on the method described by Schwertmann and Cornell (1991) using reagent-grade $\text{Fe}(\text{NO}_3)_3$. The procedure was altered slightly by slowly adding 4 M NaOH to achieve a larger specific surface area goethite. Excess salts were removed by electro dialysis until the conductivity of the wash solution was nearly equal to that of distilled, deionized water. The goethite was subsequently washed with 0.01 M HNO_3 to remove any remaining amorphous Fe phases (*e.g.* ferrihydrite). The clean goethite was freeze dried and analyzed by X-ray diffraction (XRD) and thermogravimetric analysis (TGA), and the results were characteristic of goethite. The ratio of Fe extracted by ammonium oxalate (in the dark) to total iron (Fe_0/Fe_t) was used to determine the presence of remaining amorphous phases (Schwertmann *et al.*, 1985). The Fe_0/Fe_t ratio was 0.0023, indicating essentially complete conversion of ferrihydrite to goethite. The specific surface area was $87 \text{ m}^2\text{g}^{-1}$ as determined by a five-point N_2 Brunauer-Emmett-Teller (BET) gas adsorption isotherm method.

Adsorption envelopes

Adsorption of phosphate, molybdate, selenite and EDTA was 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 g L^{-1}). Adsorption envelopes 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. An appropriate quantity of goethite (0.75 g) and NaNO_3 were added to the batch reactor, dispersed with a sonic dismembrator, and adjusted to pH 10 using an automatic titrator (Metrohm 718 Stat Titrimo, 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., Warton, Ontario, Canada) spinning at $\sim 5 \text{ rev s}^{-1}$ and allowed to equilibrate for 15 h at a constant temperature of $298 \pm 0.1 \text{ K}$.

After $\sim 15 \text{ h}$, an appropriate quantity of a 0.01 M stock solution of phosphate, molybdate, selenite or EDTA (as Na 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. Samples of ~ 6 – 10 mL samples were removed from the suspension and filtered through a $0.25 \mu\text{m}$ membrane (Millipore). This procedure was repeated at different pH values (10–3) to obtain an adsorption envelope. 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, Al 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, Massachusetts) inductively coupled plasma-atomic emission spectrometer (ICP-AES). The EDTA was analyzed using a Dohrmann 180 (Dohrmann, Santa Clara, CA) organic C analyzer.

Dissolution experiments

All dissolution studies were carried out using a pH-stat technique in the presence of 1 mM EDTA. An appropriate quantity (0.75 g) of freeze-dried goethite was weighed carefully into a 500 mL teflon liner and 250 mL of 0.01 M NaNO_3 were 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 stirred well 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 2 h, after which the EDTA (1 mM) was added to the suspension. Sampling began 1 h after the EDTA was added and continued for $\sim 50 \text{ h}$. Dissolution rates were obtained from the linear part of the dissolution

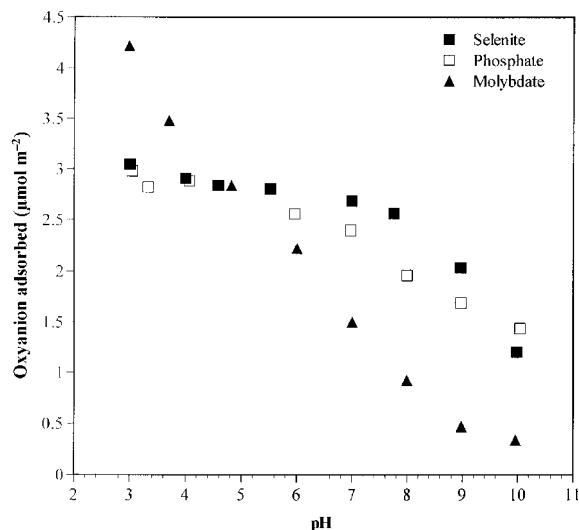


Figure 1. Adsorption of selenite (SeO_3^{2-}), molybdate (MoO_4^{2-}) and phosphate (PO_4^{3-}) on $\alpha\text{-FeOOH}$. $\alpha\text{-FeOOH}$ suspension density = 2.5 g L^{-1} , $[\text{SeO}_3^{2-}] = [\text{MoO}_4^{2-}] = [\text{PO}_4^{3-}] = 1.0 \text{ mM}$, ionic strength = 0.01 M NaNO_3 .

experiment (>10 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. The Fe was analyzed using a SpectroFlame FTMOA85D ICP-AES.

RESULTS AND DISCUSSION

Adsorption envelopes

Phosphate, selenite and molybdate adsorption on goethite decreased as pH increased (Figure 1). These results are consistent with other research examining oxyanion adsorption on goethite (Hingston *et al.*, 1972; Bibak and Borggaard, 1994; Goldberg and Forster, 1998). No significant difference was observed between the experiments conducted at 0.01 M and 0.001 M NaNO_3 , which, along with spectroscopic and kinetic data, indicates inner-sphere adsorption (Tejedor-Tejedor and Anderson, 1986; Zhang and Sparks, 1989; Bibak and Borggaard, 1994). Molybdate exhibits a much steeper adsorption envelope than either phosphate or selenite, which have very similar trends. The differences in the slope of the adsorption envelopes between oxyanions can be related to the degree of protonation of the molecule. In general, triprotic acids exhibit a much broader adsorption envelope 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).

Similar to the oxyanions, EDTA is also most strongly adsorbed at lower pH values (Figure 3), which corresponds to its pK_{a1} value of 2.0 (Weast, 1986). This trend is consistent with other studies examining EDTA adsorption on Fe oxides (Rueda *et al.*, 1985; Bondietti

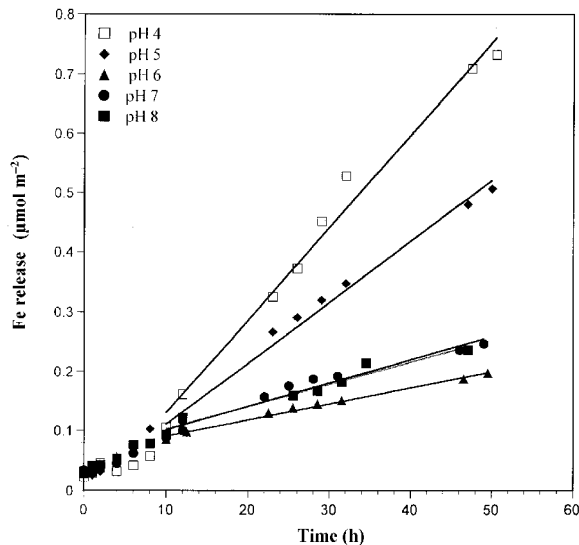


Figure 2. Fe release at different pH values over time in the presence of EDTA. $\alpha\text{-FeOOH}$ suspension density = 2.5 g L^{-1} , $[\text{EDTA}] = 1.0 \text{ mM}$, ionic strength = 0.01 M NaNO_3 .

et al., 1993; Nowack and Sigg, 1996). The magnitude of EDTA adsorption is 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).

Dissolution studies

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 2; Table 1). Dissolution rates were greatest at pH values of

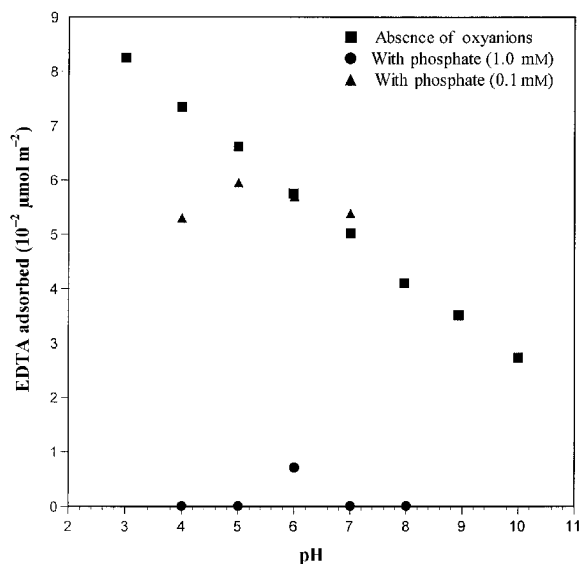


Figure 3. Comparison of EDTA adsorption in the absence and in the presence of phosphate. $\alpha\text{-FeOOH}$ suspension density = 2.5 g L^{-1} , $[\text{EDTA}] = 1.0 \text{ mM}$, $[\text{Phosphate}] = 1.0 \text{ mM}$ and 0.1 mM , ionic strength = 0.01 M NaNO_3 .

Table 1. Dissolution rates for the EDTA-promoted dissolution of goethite (2.5 g L⁻¹, 0.01 M NaNO₃, 1.0 mM EDTA).

Oxyanion or ligand concentration (mM)	pH of the solution	Dissolution rate (R_{EDTA}) $\mu\text{mol m}^{-2} \text{h}^{-1} \times 10^{-5}$
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

4 and 5 and approximately four times slower at pH values ≥ 6 . Other studies have also shown strong pH-dependent dissolution rates, although their trends varied with pH (Chang and Matijevic, 1983; Bondiotti *et al.*, 1993; Nowack and Sigg, 1997). It has been suggested that these observed trends are associated with the type of surface complex formed by the EDTA molecule, with mononuclear complexes enhancing dissolution and multinuclear complexes being associated with slow dissolution rates (Stumm, 1997).

Bondiotti *et al.* (1993) found a similar trend for the EDTA-promoted dissolution of lepidocrocite (γ -FeOOH). The rate determined at pH 3 ($30.8 \times 10^{-2} \mu\text{mol m}^{-2}\text{h}^{-1}$) is nearly double the rate found at pH 7 ($15.4 \times 10^{-2} \mu\text{mol m}^{-2}\text{h}^{-1}$). These results are contrary to those determined by Nowack and Sigg (1997) who observed a nearly constant rate from pH = 3–7 ($\sim 3.0 \times 10^{-3} \mu\text{mol m}^{-2}\text{h}^{-1}$) and then a maximum rate at pH = 8 ($\sim 8.2 \times 10^{-3} \mu\text{mol m}^{-2}\text{h}^{-1}$). Chang and Matijevic (1983) found an increased rate of the EDTA-promoted dissolution of hematite (α -Fe₂O₃) at pH = 7.4 ($41.7 \times 10^{-3} \mu\text{mol m}^{-2}\text{h}^{-1}$) as opposed to pH = 3 ($6.0 \times 10^{-3} \mu\text{mol m}^{-2}\text{h}^{-1}$). We determined a maximum dissolution rate at pH = 4 of $15.8 \times 10^{-3} \mu\text{mol m}^{-2}\text{h}^{-1}$, and a minimum rate at pH = 6 of $2.7 \times 10^{-3} \mu\text{mol m}^{-2}\text{h}^{-1}$ (Table 1). 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 Fe promoting reductive dissolution pathways, and the presence of amorphous phases in the oxides synthesized for the studies.

EDTA with oxyanions. The addition of 1 mM of phosphate, molybdate and selenite inhibited the EDTA-promoted dissolution of goethite at all pH values (Figure 4). Based on the number of reactive functional groups available ($5.7 \mu\text{mol sites m}^{-2}$) for oxyanion adsorption on goethite, and the assumption that bidentate surface complexes predominate for the oxyanions, there would be relatively few sites remaining for EDTA to adsorb and hence promote dissolution (Parfitt, 1978; Hiemstra and van Riemsdijk, 1996). This is supported by analytical data which show almost no EDTA adsorption in the presence of the oxyanions at 1 mM. A comparison of EDTA adsorption alone and in the presence of phosphate is displayed in Figure 3. 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

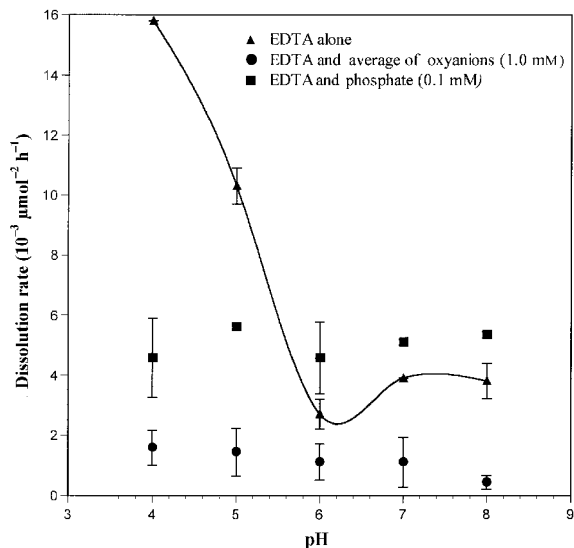


Figure 4. Comparison of the dissolution rates in the presence of EDTA and EDTA with the oxyanions at 1.0 and 0.10 mM. α -FeOOH suspension density = 2.5 g L⁻¹, [EDTA] = 1.0 mM, [oxyanions] = 1.0 mM or 0.10 mM, ionic strength = 0.01 M NaNO₃.

reducing EDTA adsorption (McKenzie, 1983; Eick *et al.*, 1999).

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 4), the influence of these oxyanions was examined at just two pH values, 4 and 6. We propose at pH values of 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 are present at a concentration of 1.0 mM at these same pH values, EDTA adsorption is inhibited, and dissolution rates are reduced significantly. When the oxyanion concentrations are reduced to 0.1 mM, goethite surface sites are available for EDTA adsorption and the dissolution rate increases compared to dissolution in the presence of the oxyanions at 1 mM (Figure 4). 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.

In the absence of oxyanions, EDTA adsorbed as a multinuclear complex at pH values ≥ 6 , which inhibited the dissolution rate compared to lower pH values. In the presence of oxyanions at 1.0 mM, EDTA adsorption was insufficient to promote dissolution, 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 4). 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 3). In order for the same amount of EDTA to adsorb in the presence of 0.1 mM oxyanions, we propose that the adsorption of the oxyanions causes a reduction in the number of surface sites available for EDTA adsorption. This shifts the EDTA conformation from a multinuclear complex to a mononuclear 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.

The adsorption data for the oxyanions at pH 6 at both concentrations support this hypothesis. At 1.0 mM, the oxyanions occupied ~ 5.0 $\mu\text{mol sites m}^{-2}$ of the total goethite surface sites available for oxyanion adsorption (5.7 $\mu\text{mol sites m}^{-2}$) (Hiemstra and van Riemsdijk, 1996). 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 1) (Parfitt, 1978; Manceau and Charlet, 1994; Eick *et al.*, 1999). The EDTA adsorption was inhibited due to a lack of available surface sites. When the oxyanion concentration was decreased to 0.1 mM, they occupied 0.5 $\mu\text{mol sites m}^{-2}$, which would be 1.0 $\mu\text{mol sites m}^{-2}$ assuming bidentate surface coverage. This accounts for less than half of the total available sites, which promotes EDTA adsorption as a mononuclear (dissolution-enhancing) surface complex. Bondietti *et al.* (1993) also found that decreasing the concentration of the oxyanion promoted the dissolution of lepidocrocite. At pH 7 with EDTA and phosphate at equivalent concentrations, the dissolution rate was 46.2×10^{-3} $\mu\text{mol m}^{-2}\text{h}^{-1}$. As the phosphate concentration was decreased by one order of magnitude, the rate increased to 76.9×10^{-3} $\mu\text{mol m}^{-2}\text{h}^{-1}$. These results are consistent with the results of Borggaard (1991) and Eick *et al.* (1999) and demonstrate that dissolution of oxide surfaces is not directly affected by the type of surface complex formed by the oxyanion but rather by the number of sites occupied by the oxyanions. However, depending upon surface coverage, the oxyanions may alter the type of surface complex formed by the organic ligand hence inhibiting or enhancing dissolution relative to the organic ligand alone.

CONCLUSIONS

From an examination of the influence of phosphate, selenite and molybdate on the EDTA-promoted dissolution of goethite, we propose that the type of surface complex formed by the oxyanions is not responsible for the changes in dissolution rates. However, the oxyanions can indirectly influence dissolution by affecting the type of EDTA surface complex. At pH values where EDTA

forms a mononuclear (dissolution-enhancing) surface complex, adsorption of oxyanions reduces EDTA adsorption, and this 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 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 is important if we are to understand weathering and Fe cycling in natural systems. This may be especially meaningful in natural systems where plants and microbes secrete multidentate ligands referred to as siderophores, which can increase dissolution of oxide minerals and Fe availability.

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