Steady-State Dissolution Kinetics of Aluminum-Goethite in the Presence of Desferrioxamine-B and Oxalate Ligands

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This paper reports steady-state dissolution rates of synthetic low-substitution Al-goethites (mol % Al < 10) at pH 5 in the presence of the trihydroxamate siderophore, desferrioxamine B (DFO-B), and the common biological ligand, oxalate. The siderophore-promoted Fe release rate increased both with the level of Al substitution and with DFO-B concentration up to about 100 μ M, after which a plateau occurred, suggesting a saturation effect from DFO-B adsorption as a precursor to dissolution. At concentrations above 200 μ M, oxalate also enhanced the Fe release rate, which however was not influenced by Al substitution. For Al-goethites with mol % Al < 4, the Fe release rate in the presence of 40 μ M DFO-B together with varying concentrations of oxalate was typically greater than the corresponding sum of dissolution rates in the presence of the two ligands alone. This synergism may be the combined result of the ability of oxalate to adsorb strongly at the goethite surface, thus promoting Fe release, and of the high selectivity of DFO for Fe(III). Ferric oxalate complexes formed during dissolution will likely lose Fe^{3+} by ligand substitution with DFO-B, leading to the production of $\text{Fe}(\text{HDFO-B})^+$ and uncomplexed oxalate, the latter of which, in turn, could adsorb to the goethite surface again. For Al-goethites with mol % Al > 4, synergism was not apparent, which may signal the effect of a decreased surface density of Fe–OH sites associated with Al for Fe substitution. The oxalate-promoted release rates of Al did not scale with those of Fe, indicating incongruent dissolution. However, Al release rates in the presence of DFO-B did scale approximately with those of Fe but were not affected by the concentration of siderophore. These results are consistent with the presence of $\text{Al}(\text{OH})_3$ inclusions in Al-goethite.

Introduction

Goethite formed in terrestrial weathering environments often exhibits Al substitution for Fe, $[\text{Fe}_{1-x}\text{Al}_x\text{OOH}]$, with Al content up to $x = 0.33$ (1). X-ray diffraction analyses of more than 200 South African soil samples collected by Fitzpatrick and Schwertmann (2) indicated the predominance of goethite with low Al content ($x < 0.15$) in hydromorphic environments. This level of substitution, characteristic of variable redox

conditions at circumneutral pH, alters crystal size, texture, domain morphology, surface area, structural strain, and other structural properties (1, 3) that influence the rates and mechanisms of goethite dissolution. Schwertmann and co-workers (4, 5) have reported that low Al substitution for Fe in goethite also leads to a decrease in proton- and ligand-promoted reductive dissolution rates, concluding that this occurs because of an increase in disorder of the crystals within interdomains, leading to fewer structural defects that promote abiotic dissolution (1).

A recent study of the microbial reductive dissolution of synthetic Al-goethites ($x = 0, 0.051$, and 0.33) by *Clostridium butyricum*, an Fe-reducing bacterium isolated from an oxisol, showed incongruent dissolution of Al and Fe, unlike abiotic reductive dissolution, and a decrease in the rate of Fe release by reductive dissolution as Al substitution increased (6). The decrease in Fe release rate was attributed to the accumulation of Al at the goethite surface resulting in the blocking of reactive sites during enzymatic reduction. However, another study of the microbial reductive dissolution of a natural Al-goethite sample ($x = 0.17$; 7) by *Shewanella putrefaciens* found that Al sorption had no effect on dissolution. This latter result was explained by Al adsorption or precipitation at surface sites distant from those where reductive dissolution occurred.

The bacterially mediated dissolution of Al-goethite in oxic environments also has been investigated recently. Samples of synthetic Al-substituted goethite ($0 \leq x \leq 0.088$) incubated under batch conditions (8) with siderophore-producing bacteria (*Pseudomonas mendocina* var.) showed microbial release of Fe that was inversely related to the particle aspect ratio and, therefore, increased with increasing Al content, in contrast with reductive dissolution. Evidently, Al substitution leads to an increase in the population of reactive sites available for microbially mediated dissolution under oxic conditions. Under reducing conditions, the opposite appears to be true. For example, in the dissolution of goethite by *C. butyricum* (6), although the number of electrons produced by glucose fermentation in the presence of Al-goethite was comparable to the number produced in the presence of unsubstituted goethite, the percentage use for Fe(III) reduction was 5.7% for unsubstituted goethite, but only 1.6 and 0.55% for Al-goethites with $x = 0.05$ and 0.33 , respectively. Thus, the number of ferric reduction sites, not metabolic activity, appeared to limit the release of Fe during the reductive dissolution of Al-goethite.

Aluminum substitution has been shown to affect the release of Fe from goethite during either microbially mediated (6–8) or ligand-promoted (1) dissolution, but the details of surface–organic interactions associated with these processes remain unexplored. Of particular interest for the present study is the fact that, although the biotic dissolution of Fe(III)-bearing minerals under oxic conditions is accompanied by the production of siderophores (9, 10), little quantitative information exists about their specific role in the dissolution process. In pioneering experiments with unsubstituted goethite, Watteau and Berthelin (9) demonstrated the remarkable efficacy of the common trihydroxamate siderophore, desferrioxamine B (DFO-B), in promoting the solubilization of Fe, when compared to either protons or other common biological ligands, such as oxalate. They attributed this difference to the Fe(III)-specific complexing ability of the siderophore. Similarly, Kraemer et al. (11) reported an enhanced rate of Fe release from goethite in the presence of DFO-B, concluding that coordination of the siderophore to an Fe(III) center at the mineral surface is a precursor to the dissolution process, a mechanistic step also suggested by

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TABLE 1. Properties of the Al-Goethite Samples

sample	mol % Al ^a (=100×)	a _s ^b (m ² g ⁻¹)	ln K ^c (K in min ⁻¹)	α ^c	ln k ^c (k in min ⁻¹)
S1	2.6 ± 0.7	46.8 ± 3.9	-7.76 ± 0.98	1.22 ± 0.14	-6.3 ± 0.3
S2	3.6 ± 1.2	44.9 ± 3.8	-7.76 ± 0.59	1.06 ± 0.09	-6.7 ± 0.2
S3	4.5 ± 1.1	39.5 ± 3.4	-10.15 ± 1.55	1.32 ± 0.21	-7.7 ± 0.3
S4	10 ± 2	37.0 ± 3.2	-11.85 ± 1.85	1.41 ± 0.22	-8.5 ± 0.3

^a Measured by HCl digestion of the Al-goethite samples. Determinations of Al and Fe in triplicate for each of two samples of Al-goethite.

^b Measured by the static BET method; mean ± standard deviation. ^c Parameters in eq 2 (time in min) with *P* = 0.05 confidence intervals.

Holmén and Casey (12, 13) and by Kalinowski et al. (10) in their studies of the kinetics of hydroxamate-promoted mineral dissolution.

Organic ligands of small size and low molecular mass commonly found in soils, such as oxalate, may also enhance the dissolution of goethite (e.g., ref 14). How the presence of oxalate, DFO-B, or both ligands affects Fe release following dissolution remains largely unknown. Cheah et al. (15) very recently have shown that the dissolution rate of unsubstituted goethite at pH 5 in the presence of DFO-B ([DFO-B] ≤ 80 μM) was doubled in the presence of oxalate ([Ox] = 29 or 40 μM), whereas the dissolution rate in the presence of oxalate ([Ox] = 0–200 μM) was increased by an order of magnitude when DFO was present at 40 μM solution concentration. These results were thought to imply that if DFO-B were present at large enough concentration to complex all dissolved Fe(III) released by oxalate-promoted goethite dissolution, it could displace oxalate from Fe–oxalate complexes that may have formed and, as a result, enable the uncomplexed oxalate ligand to react again with the goethite surface. The resulting synergy in the two-ligand system then suggests that the production of siderophores in the presence of low concentrations of oxalate would be an extremely effective mechanism for the microbial acquisition of Fe from goethite.

In this paper, we extend the study of Cheah et al. (15) to dissolution experiments with low-substitution Al-goethite (*x* < 0.1) at pH 5 in the presence of both the trihydroxamate siderophore DFO-B and the ubiquitous biological ligand oxalate. The objective of our experiments was to quantify the dissolution kinetics of Al-goethite as influenced by the siderophore, by oxalate, and by the two ligands in combination under steady-state conditions. A broad range of concentrations of the two ligands was utilized (20–1000 μM) to encompass their expected concentrations in soil solutions (9).

Experimental Section

Materials. Perchloric acid (70%), sodium hydroxide (1 M), aluminum nitrate (99+%), ferric nitrate (99%), potassium hydroxide (99%), and hydrochloric acid (30%) were purchased from Fisher (Fair Lawn, NJ). Sodium perchlorate (ACS grade) was purchased from GFS (Columbus, OH); oxalic acid (99+%) was purchased from Aldrich (Milwaukee, WI). 2-(*N*-Morpholino)ethanesulfonic acid buffer (MES) was purchased from Sigma (St. Louis, MO). Iron and aluminum ICP standard solutions were purchased from Ultra Scientific (North Kingston, RI). Desferrioxamine B (DFO-B) was produced by Ciba-Geigy (Desferal) and received as a gift from Salutar Corporation. In all experiments, solutions were prepared with high-purity 18 MΩ·cm water (Milli-Q Plus, Millipore, Ann Arbor, MI).

Synthesis. Four samples of Al-substituted goethite (S1–S4) were synthesized as described in Schwertmann and Cornell (3). Fresh solutions of 1 M Fe(NO₃)₃, 0.5 M Al(NO₃)₃, and 5 M KOH were prepared. An aluminate solution was prepared by adding 500 mL of Al(NO₃)₃ and 300 mL of KOH

solutions at constant stirring. Aliquots of aluminate solution (20, 40, 80, and 120 mL, respectively) were poured into 2-L polypropylene bottles followed by 178, 176, 170, and 165 mL of KOH stock solution. Immediately after that, 100 mL of the Fe(NO₃)₃ stock solution was added to each bottle and made up to 2 L with twice-distilled water. The polyethylene tubes were mixed for 10 min and placed in an oven at 70 °C for 14 days. The bottles were shaken once a day. After crystallization was complete (as indicated by a compact yellow precipitate), the samples were centrifuged, and the product was washed twice with 400 mL of 1 M KOH to remove extra Al. The pH of the supernatant solution was adjusted to 7.5 with 1 M HCl, washed with twice-distilled water, freeze-dried, and stored in polyethylene bottles. These four samples will be referred to as S1–S4. Powder X-ray diffraction (Cu Kα) confirmed the four synthesized solids as Al-goethites (data not shown) with characteristic peaks assigned to the 110, 120, 130, 111, 140, 221, 151, 250, and 061 planes. The progressive shifting of the 130, 061, 221, and 120 peaks to lower *d* values with increasing sample number confirmed an increasing substitution of Fe by Al (1, 16). Additional confirmation of Al substitution was provided by ATR-FTIR spectra of the samples (data not shown), which displayed a blue-shift of the OH bending vibrational bands with increasing sample number, typical of increasing Al content (1, 3).

Characterization of the Al-Goethite Samples. The nominal Al content of the Al-goethite samples was determined from acid digestion (Table 1). Specific surface area (a_s) determinations on the goethite samples were performed by the static BET method using N₂ gas. In addition, HCl dissolution kinetics studies were conducted to characterize Al substitution and crystallinity (17) in the four Al-goethite samples.

HCl Digestion. Aluminum determination by complete dissolution in concentrated HCl was performed as described by Schwertmann (3, 18). A total of 100 mg of Al-goethite sample was incubated with 20 mL of 12 N HCl at 80 °C for 20–40 min or until total dissolution was achieved. The solutions were diluted 1:100 with acidified twice-distilled water (10% HCl) and analyzed for Al and Fe using an inductively-coupled plasma atomic emission spectrometer (ICP-AES, Thermo Jarrel Ash) with emission lines at 396.1 and 238.2 nm, respectively.

HCl Dissolution Kinetics. Acid dissolution kinetics studies of the Al-goethite samples were conducted as described by Schwertmann (4). Briefly, 250-mg samples of goethite were dissolved in 250 mL of 6 M HCl at 24 °C with constant shaking. Subsamples of the reaction mixture were taken at intervals over a period of 72 h or until total dissolution was achieved and then centrifuged. The supernatant solution was decanted and filtered prior to Fe analysis using ICP-AES at 238.2 nm.

The fraction of Fe dissolved was plotted as function of reaction time for each of the samples, where “fraction of Fe dissolved” refers to the amount of Fe dissolved at a time *t* relative to the amount of Fe dissolved at *t* = 72 h. The resulting S-shaped dissolution curves (not shown) were modeled, similar to a large number of dissolution experiments on iron oxides (ref 1, p 296), by the Kabai (19) equation, based on

the concentration–time relationship:

$$C(t) = 1 - e^{-Kt/\alpha} \quad (1)$$

or in log-transform linearized form:

$$\ln \{ \ln [1/(1 - C)] \} = \ln K + \alpha \ln t \quad (2)$$

where $C(t)$ is the fraction of Fe dissolved at time t , and K and α are empirical constants. The regression parameters ($\ln K$, α) and the dissolution rate constant k [$k = (1/\alpha) \ln K$] found for the four samples are listed in Table 1 (ANOVA with 95% confidence intervals).

Determination of Al content using the Vegard rule (20) based on the two strongest XRD reflections, $d(110)$ and $d(111)$, as calculated from the diffractograms of samples S1–S4, and the c -dimension of the unit cell was considered but not included because the Al content must differ between samples by at least 5.2 mol % Al (20) to be distinguished by this method.

Ligand-Promoted Dissolution Kinetics. Continuous-flow stirred-tank reactors (CFSTR) were used to study dissolution (one Al-goethite sample per reactor) in the presence of DFO-B and oxalate ligands. The CFSTR apparatus (Cole-Parmer, Catalogue No. E-02910-41) was similar to that described by Kraemer and Hering (21). The body of the reactor was made from Plexiglass, while the cap and bottom were made from Delrin. The volume of the reactor was 69.5 ± 0.2 mL. Cellulose–acetate (Millipore) filters ($0.025 \mu\text{m}$) were placed at the bottom of each reactor before adding goethite (0.69 g); the reactors were then filled with distilled water, such that the final suspension contained 10 g L^{-1} goethite. The reactors were closed, and Tygon tubing (replaced monthly) was used to connect the reactors with the corresponding influent and effluent solution containers. Special caution was taken to prevent the formation of air bubbles in the reactors and Tygon lines. The flow rate of the influent solution was controlled using a peristaltic pump (Masterflex), and the reactors were stirred at constant speed of about 500 rpm.

The influent solution was adjusted to pH 5 by adding aliquots of HNO_3 or NaOH stock solution. Its composition was 0.01 M NaClO_4 , 5 mM MES buffer, oxalate (0 – $1000 \mu\text{M}$), and/or DFO-B (0 – $2000 \mu\text{M}$). To promote dissolution of labile Fe, the Al-goethite samples were preconditioned with influent solution at pH 5 containing $20 \mu\text{M}$ DFO-B for 400 h or until the Fe concentration in the effluent solution was observed to be invariant over time. During pretreatment, non-steady-state conditions prevailed, wherein dissolved concentrations of DFO-B and Fe varied continuously. The difference in the influent and effluent DFO-B concentrations was very small, indicating that very little DFO-B (if any) had become irreversibly bound to the goethite surface. Then the concentration of the influent DFO-B was reduced to zero, and the samples were equilibrated for an additional 120 h. Thereafter, the dissolution kinetics of the goethite samples were studied as function of the concentration of DFO-B or oxalate added initially to the influent suspension, namely, $[\text{DFO}]_0$ or $[\text{Ox}]_0$, respectively. A third set of experiments was performed to study the effect of $[\text{Ox}]_0$ on the dissolution of Al-goethites by $[\text{DFO}]_0$, with $[\text{DFO}]_0 = 40 \mu\text{M}$ and $[\text{Ox}]_0$ varied from 0 to $1000 \mu\text{M}$. Proton activity was measured with a Ross combination electrode calibrated with buffer solutions at pH 4, pH 7, and pH 10.

The entire system, including influent and effluent solution containers, lines, and pumps, was covered with aluminum foil. Samples of the effluent solution of each reactor were collected twice per day in disposable polyethylene tubes and stored at 5°C for Fe and Al determination using ICP-AES. Standard curves, freshly prepared, were used for the quantitation of Fe and Al. A third sample was collected daily to measure the effluent flow rate.

The dissolution rate of Al-goethite (R), determined after steady values of the Fe concentration in the effluent solution were observed (>500 h), was calculated as

$$R = 60[\text{Fe}]_{\text{eff}} \frac{q}{m} \quad (3)$$

where $[\text{Fe}]_{\text{eff}}$ is the concentration of Fe in the effluent solution (μM) under steady-state conditions, q is the effluent flow rate (mL min^{-1}), and m is the mass of goethite (g). The resulting units of R are then $\text{nmol g}^{-1} \text{ h}^{-1}$. (The number 60 in eq 3 serves to convert the rate to an hourly basis). Typical effluent flow rates ranged between 0.08 and 0.16 mL min^{-1} . The value of $[\text{Fe}]_{\text{eff}}$ used was the average of replicate values of Fe concentration (10 per experiment) measured in the collected samples. Conventional statistical analysis was performed to test for outliers (22). Any $[\text{Fe}]_{\text{eff}}$ values suspected as outliers were discarded when they differed by more than twice the standard deviation from the average $[\text{Fe}]_{\text{eff}}$ based on all of the remaining values determined in an experiment. The smallest value of $[\text{Fe}]_{\text{eff}}$ detectable was about $0.01 \mu\text{M}$, which leads to a minimum detectable dissolution rate of approximately $0.1 \text{ nmol g}^{-1} \text{ h}^{-1}$.

The measured dissolution rate of goethite in the presence of DFO-B and oxalate together, $R_{\text{DFO-Ox obs}}^{\text{Fe}}$, was compared to the sum of dissolution rates of goethite in the presence of DFO-B only or oxalate only, $R_{\text{DFO-Ox sum}}^{\text{Fe}}$, by using conventional statistical analysis (22) to test for significant difference ($P = 0.05$).

Results and Discussion

The HCl dissolution curves (not shown) of the Al-goethite samples were S-shaped, while the dissolution rate decreased and the shape of the curve became increasingly sigmoidal with increasing Al for Fe substitution, as also described by Schwertmann (1, 4, 18). Electron micrographs (23) of a series of low-substitution Al-goethites ($x < 0.1$) before and after dissolution in 6 M HCl at 24°C revealed increases in surface area during the initial stages of dissolution and preferential dissolution of less-ordered portions of the goethite crystals. The shapes of the dissolution curves for samples S1–S3 were consistent with the concept that surface defects and inter-domain boundaries may be exposed by etching during the initial stages of dissolution (18, 24) and, as result, increase the surface area available to proton-promoted dissolution. The dissolution curve for sample S4 had a pronounced sigmoidal shape, which could be because of decreased surface density of Fe–OH sites (24) following Al for Fe substitution in goethite.

Table 1 shows that the dissolution rate constant k (eq 2) decreased with increasing Al content, in agreement with the well-known observation that Al substitution decreases proton-promoted dissolution (1, 4). The decrease in k with a decrease in surface area (Table 1) would suggest that the acid dissolution of samples S1–S4 is surface-controlled. Figure 1 shows that the dissolution rate per unit surface area (k/a_s) also tends to decrease with increasing Al substitution, in good agreement with data for synthetic goethite samples and Fe-rich goethitic/hematitic tropical soils (4). The results shown in Figure 1 can be explained by considering the combined effect of surface area and Al substitution on the dissolution of samples S1–S4, as described by Ruan and Gilkes (24). Aluminum substitution in goethite leads to a reduction in crystal size and surface area, but acid digestion of Al-goethite favors the cleavage of Fe–O bond(s) more than Al bond(s). Figure 1 thus indicates the dominance of the effect of the greater strength of the Al–O bond in the acid dissolution of samples S1–S4.

Ligand-Promoted Dissolution. The Fe release rate from Al-goethite ($R_{\text{DFO}}^{\text{Fe}}$, Figure 2 and Table 2) increased as the

FIGURE 1. Comparison of area-normalized dissolution rate constants as a function of Al substitution for samples S1–S4 (●) with the same data for soil goethites (○; 4).

FIGURE 2. Steady-state dissolution rates ($R_{\text{DFO}}^{\text{Fe}}$ in $\text{nmol g}^{-1} \text{h}^{-1}$) of unsubstituted goethite (○) and Al-goethite samples S1 (●), S2 (+), S3 (x), and S4 (Δ) plotted as a function of the concentration of DFO-B (Table 2).

TABLE 2. Steady-State DFO-Promoted Dissolution Rates^a

[DFO-B] ₀ (μM)	sample				
	unsubstituted ^b	S1 ^c	S2 ^c	S3 ^c	S4 ^c
20	11	3	3	5	3
40	18	11	9	33	92
60	...	43	38	30	114
80	20	46	34	32	117
100	...	...	34	38	190
200	...	45	51	117	200
500	...	...	94	107	1039
1000	...	35	37	25	1129

^a $R_{\text{DFO}}^{\text{Fe}}$ in $\text{nmol g}^{-1} \text{h}^{-1}$. Conditions: 10 g L^{-1} goethite, 0.01 M NaClO_4 , 5 mM MES , $\text{pH } 5$. ^b Data from Cheah et al. (15). ^c Average CV = 11% for samples S1–S4. ^d (...) = not measured.

DFO-B concentration increased, exceedingly so for sample S4 ($x = 0.1$). The more modest enhancement for the less-substituted samples (S1–S3) is in keeping with available Fe release data for unsubstituted goethite (15), which showed an increase in $R_{\text{DFO}}^{\text{Fe}}$ from 11 to 20 $\text{nmol g}^{-1} \text{h}^{-1}$ with an increase in $[\text{DFO}]_0$ from 20 to 80 μM (Table 2 and Figure 2).

TABLE 3. Steady-State Oxalate-Promoted Dissolution Rates^a

[Ox] ₀ (μM)	sample				
	unsubstituted ^b	S1 ^c	S2 ^c	S3 ^c	S4 ^c
20	0	0.7	0.8	0.5	0.3
50	0.5 ^d	0.1	0.1	...	...
100	5.2	<0.1	0.1	2	3
200	18	8	17	140	15
500	50 ^e	151	45	123	67
	63 ^e				
1000	78 ^f	99	143	83	67

^a $R_{\text{Ox}}^{\text{Fe}}$ in $\text{nmol g}^{-1} \text{h}^{-1}$. Conditions: 10 g L^{-1} goethite, 0.01 M NaClO_4 , 5 mM MES , $\text{pH } 5$. ^b Data from Cheah et al. (15). ^c Average CV = 20% for samples S1–S4. ^d $[\text{Ox}]_0 = 40 \mu\text{M}$. ^e $[\text{Ox}]_0 = 800 \mu\text{M}$. ^f $[\text{Ox}]_0 = 1200 \mu\text{M}$. ^g (...) = not measured.

For samples S1–S4, there was a tendency of the Fe release rate to plateau and even decrease with increasing $[\text{DFO}]_0$, the plateau occurring at higher concentrations as the Al content of the sample increased (Figure 2). This same tendency to plateau was observed by Cheah et al. (15) for Fe release from unsubstituted goethite by DFO-B, for which a plateau was achieved when $[\text{DFO}]_0 = 20 \mu\text{M}$. Congruency of their graphs of the mass-normalized dissolution rate and the surface excess of DFO-B plotted against $[\text{DFO}]_0$, was interpreted by Cheah et al. (15) as evidence for DFO-promoted dissolution. In the present experiments, the data in Table 2 suggest that a plateau in $R_{\text{DFO}}^{\text{Fe}}$ occurs at $[\text{DFO}]_0 \lesssim 100 \mu\text{M}$, sometimes followed by a narrow plateau at $[\text{DFO}]_0 \lesssim 500 \mu\text{M}$. The values of $R_{\text{DFO}}^{\text{Fe}}$ for $[\text{DFO}]_0 \lesssim 80 \mu\text{M}$ are substantially higher for S4 than for unsubstituted goethite (Table 2; 15) and for samples S1–S3, indicating significant accessibility of DFO-B to reactive Fe(III) centers on the mineral surface.

The data on oxalate-promoted dissolution (Table 3) present a different trend. Either an inhibitory effect or no effect of the ligand was observed at low concentrations ($[\text{Ox}]_0 < 200 \mu\text{M}$), whereas enhanced dissolution occurred at higher concentrations. These results are comparable to those obtained for unsubstituted goethite (15), which show that the Fe release rate at $[\text{Ox}] < 200 \mu\text{M}$ did not surpass $18 \text{ nmol g}^{-1} \text{h}^{-1}$, and increases in $[\text{Ox}]$ from 200 to $2000 \mu\text{M}$ led to a nonlinear increase in the Fe release rate from 18 to $125 \text{ nmol g}^{-1} \text{h}^{-1}$. Within experimental precision, the values of $R_{\text{Ox}}^{\text{Fe}}$ for $[\text{Ox}]_0 = 1 \text{ mM}$ (bottom row) are mutually similar for all samples. Maurice et al. (8) also noted similar Fe release rates for unsubstituted and low-substitution Al-goethites ($x \leq 0.04$) at pH 3 in the presence of 1 mM oxalate, but they found significantly greater extent of Fe release and greater oxalate adsorption by Al-goethite containing $8.8 \text{ mol } \%$ Al, which is comparable to the Al content of sample S4. The same trend with increasing Al content was seen by Maurice et al. (8) in absorbance measurements of the maximum population of siderophore-producing bacteria per unit surface area that were grown in the presence of the Al-goethites. Growth curves and absorbance were similar if $x \leq 0.04$, whereas growth peaked earlier and absorbance was higher for $x = 0.088$. These differences were attributed to the presence of highly reactive Fe(III) centers on the surface of the Al-goethite with $x = 0.088$ (8).

Our results thus far may be summarized by stating that both DFO-B and oxalate enhanced the rate of Fe release from Al-goethite but did not show a trend of decreasing dissolution rate with increasing Al substitution like that observed commonly for proton-promoted dissolution (see, e.g., column 6 in Table 1). At concentrations below or equal to $100 \mu\text{M}$, DFO-B effected Fe release more than did oxalate, whereas above $100 \mu\text{M}$ concentration, the same was clearly true only for sample S4 ($x = 0.1$). At higher concentrations, DFO-promoted dissolution exhibited a “plateau effect” (2, 15, 25) suggesting prior adsorption of the siderophore.

TABLE 4. Observed ($R_{\text{DFO-Ox Obs}}^{\text{Fe}}$) and Calculated ($R_{\text{DFO-Ox Sum}}^{\text{Fe}}$) Dissolution Rates in the Presence of DFO-B and Oxalate^a

[Ox] ₀ (μM)	sample							
	S1		S2		S3		S4	
	obs	calc ^c	obs	calc ^c	obs	calc ^c	obs	calc ^c
0 ^b	11	11	9	9	33	33	92	92
20	15	12	196	10	11	33	77	92
50 ^d	85	11	129	9	71	33	94	92
100	134	11	76	9	52	35	84	95
200	78	19	79	26	49	175	71	107
500	87	162	153	54	106	156	54	159
1000	60	110	320	152	167	116	92	159

^a [DFO]₀ = 40 μM. $R_{\text{DFO}}^{\text{Fe}}$ in units of nmol g⁻¹ h⁻¹. Conditions: 10 g L⁻¹ goethite, 0.01 M NaClO₄, 5 mM MES, pH 5. Average CV = 11% for all samples. ^b Data from the second row in Table 3. ^c Sum of observed rate for [Ox]₀ = 0 (first row) plus the appropriate rate in Table 4 at [Ox]₀ > 0. ^d In the presence of DFO (40 μM) and oxalate (50 μM), the observed and calculated dissolution rates of unsubstituted goethite (15) corresponds to 35.40 and 18 mol g⁻¹ h⁻¹, respectively.

Siderophore-promoted Fe release generally increased with Al substitution, parallel to what has been observed in the dissolution of Al-goethite in the presence of siderophore-producing bacteria (8) but opposite to what has been reported in the dissolution of Al-goethite ($x = 0.05$ and 0.33) in the presence of Fe(III)-reducing bacteria (6).

Table 4 lists values of $R_{\text{DFO-Ox}}^{\text{Fe}}$ measured at pH 5 in the presence of 40 μM DFO-B and increasing concentrations of oxalate. These rate data showed no significant linear correlation ($P = 0.05$) with the corresponding values of $R_{\text{Ox}}^{\text{Fe}}$ in Table 3. Thus, the presence of DFO-B was indeed important. There are also important trends with the extent of Al substitution. Sample S1 displayed a synergistic effect of the two ligands (i.e., $R_{\text{DFO-Ox Obs}}^{\text{Fe}} > R_{\text{DFO-Ox Sum}}^{\text{Fe}}$) for [Ox]₀ in the midrange of concentrations studied, whereas sample S2 displayed synergism over the entire range of [Ox]₀. Samples S3 and S4 displayed little or no synergism.

The adsorption isotherm for oxalate on unsubstituted goethite in the presence of 0.01 M NaClO₄ and 5 mM MES at pH 5 (15) shows a maximum oxalate surface excess of 42 mmol kg⁻¹ for solution concentrations above 200 μM. Adsorption isotherms for oxalate on samples S1–S4 (data not shown) indicate, just as for unsubstituted goethite, substantial adsorption of oxalate over the range of [Ox]₀ listed in Table 4. Cheah et al. (15) also reported that oxalate competes with DFO-B for sorption sites on the goethite surface, explained in part because of the larger size of DFO-B molecules ($M_r^{\text{DFO-B}} = 561.7$ Da and $M_r^{\text{Ox}} = 56$ Da), which restricts their access to the surface. The trends observed for the dissolution of samples S1 and S2 (Table 4) in the presence of DFO and oxalate at concentrations below 200 μM (perhaps as high as 500 μM for S2) is worth noting since the typical concentrations of DFO-B and oxalate in natural soil solutions are also below 200 μM (9, 26–28). The synergism found may be the combined result of the ability of oxalate to adsorb strongly at the goethite surface and promote Fe release, coupled with the high selectivity of DFO for Fe(III). Chemical speciation calculations for a mixed oxalate-DFO-B solution containing Fe(III) at pH 5 (15) confirmed that practically all Fe(III) is in the form of Fe(HDFO-B)⁺ complexes. In this scenario, the Fe(III)-oxalate formed following dissolution, primarily as Fe(C₂O₄)₃³⁻ (15), will likely release Fe³⁺ by ligand substitution with DFO-B, leading to the production of Fe(HDFO-B)⁺ and uncomplexed oxalate, which in turn, could adsorb to the goethite surface again. The efficiency of oxalate in serving as an Fe shuttle nonetheless may be limited by the number of Fe–OH sites available for dissolution or the formation of Fe–oxalate–DFO ternary complexes. For

TABLE 5. Steady-State Al Release Rates from Al-Goethite^a

ligand	sample			
	S1	S2	S3	S4
none ^a	1.6 ± 0.2	1.8 ± 0.3	... ^e	...
DFO-B ^b	1.0 ± 0.4	1.2 ± 0.3	1.7 ± 0.4	2.2 ± 0.9
oxalate ^c	2.6 ± 0.6	1.9 ± 0.6	...	...
DFO-B + Ox ^d	5.1 ± 0.5	4.8 ± 1.9	4.1 ± 0.7	2.7 ± 0.9

^a R_{H}^{Al} in nmol g⁻¹ h⁻¹. Conditions: 10 g L⁻¹ goethite, 0.01 M NaClO₄, 5 mM MES, pH 5. ^b $R_{\text{DFO}}^{\text{Al}}$ in nmol g⁻¹ h⁻¹, 20–1000 μM DFO-B. ^c $R_{\text{Ox}}^{\text{Al}}$ in nmol g⁻¹ h⁻¹, 20–200 μM Ox. ^d $R_{\text{DFO-Ox}}^{\text{Al}}$ in nmol g⁻¹ h⁻¹, 40 μM DFO-B, 20–200 μM Ox. ^e (...) = not measured.

samples S3 and S4, synergism is not apparent, which may signal the effect of a decreased surface density of Fe–OH sites (24). Predominance of oxalate over DFO-promoted dissolution of samples S3 and S4 is expected because of a low DFO surface excess (ca. 2.5 ± 0.2 mmol kg⁻¹) and an increased oxalate adsorption with Al substitution for $x > 0.04$ (8). These considerations imply that there are optimal combinations of ligand concentration and Al substitution that would lead to synergism between DFO-B and oxalate. Evidently, this combination was achieved for samples S1 and S2 in the present experiments.

Table 5 lists steady-state Al release rates for the dissolution experiments whose results are described in Tables 2–4. If dissolution were congruent, then the Al release rate would scale with the Fe release rate as the ratio $x/(1 - x)$. For the four Al-goethites investigated, this ratio is nominally 0.026, 0.037, 0.047, and 0.11, respectively. Comparison of the data in Table 5 with the corresponding Fe release rates in Tables 2–4 shows that the proton- and oxalate-promoted release rates for Al are more than an order of magnitude larger than what congruent dissolution would yield. The Al release rates for samples S1, S2, and S3 in the presence of DFO-B, however, are approximately what congruent dissolution would provide ($R_{\text{DFO}}^{\text{Al}}/R_{\text{DFO}}^{\text{Fe}} = 0.025 \pm 0.008$, 0.030 ± 0.014 , 0.036 ± 0.016 , respectively), whereas that for S4 is low ($R_{\text{DFO}}^{\text{Al}}/R_{\text{DFO}}^{\text{Fe}} = 0.015 \pm 0.009$). The comparison for $R_{\text{DFO-Ox}}^{\text{Al}}$ is roughly similar. Therefore, overall, DFO-B had the effect of making Al-goethite dissolution more congruent than in the absence of ligand or in the presence of oxalate. We note in passing that samples S1 and S2 appear to show the same synergistic behavior for Al release as they exhibited for Fe release ($R_{\text{DFO-Ox}}^{\text{Al}} > R_{\text{DFO}}^{\text{Al}} + R_{\text{Ox}}^{\text{Al}}$).

As suggested by Bousserhine et al. (6), not all the Al in Al-goethite may be in solid solution with Fe, the possibility then being that gibbsite-like inclusions or coatings may have formed instead, especially if $x > 0.04$ (29, 30). This would lend itself to differing response to protons and ligands as well as to facile secondary precipitation of Al released by the dissolution of any true Al-goethite solid solution. The stability constant for the 1:1 complex of Al with deprotonated DFO-B is significantly smaller than that of Fe(III) (15, 31, 32):

The same trend holds for oxalate (33), but the difference in log K_M values is much smaller. These trends in log K_M can be attributed to Fe³⁺ being a harder, more electronegative cation ($\chi = 1.96$) than Al³⁺ ($\chi = 1.61$) and, therefore, more likely to form very stable complexes with either oxalate or DFO hard-O donor atoms (O_L). Because Al³⁺ has the lower electronegativity, it is also likely to promote less electron delocalization along O_L–Fe–O–Al units and, therefore, a lower vicinal Fe–O bond energy.

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