Mechanisms of goethite dissolution in the presence of desferrioxamine B and Suwannee River fulvic acid at pH 6.5

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Abstract

Siderophores are Fe$^{3+}$ specific low MW chelating ligands secreted by micro-organisms in response to Fe stress. Low MW organic acids such as oxalate have been shown to enhance siderophore mediated dissolution of Fe$^{3+}$ oxides. However, the effect of fulvic acid presence on siderophore function remains unknown. We used batch dissolution experiments to investigate Fe release from goethite in the goethite-fulvic acid-desferrioxamine B (goethite-SRFA-DFOB) ternary system. Experiments were conducted at pH 6.5 while varying reagent addition sequence. FTIR and UV-Vis spectroscopy were employed to characterise the Fe-DFOB, Fe-SRFA and DFOB–SRFA complexes. Iron released from goethite in the presence of SRFA alone was below detection limit. In the presence of both SRFA and DFOB, dissolved Fe increased with reaction time, presence of the DFOB-SRFA complex, and where SRFA was introduced prior to DFOB. FTIR data show that in the ternary system, Fe$^{3+}$ is complexed primarily to oxygen of the DFOB hydroxamate group, whilst the carboxylate C=O of SRFA forms an electrostatic association with the terminal NH$_3^+$ of DFOB. We propose that SRFA sorbed to goethite lowers the net positive charge of the oxide surface, thus facilitating adsorption of cationic DFOB and subsequent Fe$^{3+}$ chelation and release. Furthermore, the sorbed SRFA weakens Fe-O bonds at the goethite surface, increasing the population of kinetically labile Fe. This work demonstrates the positive, though indirect role of SRFA in increasing the bioavailability of Fe$^{3+}$.

Keywords: siderophore, goethite, dissolution, Suwannee River fulvic acid, desferrioxamine
In oxic soils and sediments, Fe availability is limited by the low solubility of Fe oxides at circumneutral pH (Raymond and Dertz, 2004). To obtain Fe from these sparingly soluble phases, low MW Fe$^{3+}$-chelating ligands known as siderophores are released by plants and micro-organisms (Haselwandter, 2008). For example, twice as much Fe is solubilised from goethite in the presence of 126 µM desferrioxamine B (DFOB), a trihydroxamate siderophore, than in the presence of 100 mM HCl at pH 3 over a 28-day reaction (Watteau and Berthelin, 1994). Furthermore, at hydroxamate siderophore concentrations typical of soils (i.e. $10^{-7}$ – $10^{-8}$ M; Powell et al., 1980), goethite solubility increases over a wide pH range (Kraemer, 2004), where the dissolution of goethite at pH > 4 is described as ligand-controlled (Holmén and Casey, 1996; Reichard et al., 2007a).

Iron(III) is coordinated to the hydroxamate groups of DFOB (Fig. 1) with Fe oxide dissolution influenced by siderophore concentration (Liermann et al., 2000), solution pH (Cervini-Silva, 2008) and temperature (Cocozza et al., 2002). As revealed by single-crystal X-ray diffraction, the chelate molecule consists of two closed loops and a free chain containing a protonated amine (Dhungana et al, 2001). The six hydroxamate oxygen atoms coordinate Fe$^{3+}$ and form a distorted octahedral geometry around the metallic centre (Cozar et al., 2006; Domagal-Goldman et al., 2009) (Fig. 1b). As a consequence of this complexation, the hydroxamate (oxime) protons are lost and the goethite hydroxyl or water groups coordinating Fe$^{3+}$ are displaced.

Iron release from goethite may be enhanced by the presence of low MW organic acids. For example, goethite dissolution by $5 \times 10^{-5}$ M oxalate, malonate or succinate at pH 6 yielded $10^{-11}$ M Fe following 400 h reaction (Reichard et al., 2007a) while the presence of citrate produced $10^{-7}$ M Fe and fumarate yielded undetectable levels of dissolved Fe. When
DFOB was added to those systems containing both goethite and low MW organic acids, greater amounts of Fe were released than in DFOB-only goethite systems. For example, soluble Fe concentrations increased from $10^{-11}$ M to $10^{-5}$ M when $5.0 \times 10^{-5}$ M DFOB was added to a goethite suspension along with equimolar concentrations of the organic ligands listed above, except for citrate, for which soluble Fe increased only marginally, from $10^{-7}$ M to $10^{-6}$ M.

Fulvic acid (FA) (Fig. 2), the acid soluble component of humic substances are, along with hydrous Fe oxides and siderophores, ubiquitous in soils and sediments (Stevenson, 1985). Fulvic acid sorbs strongly to goethite surfaces at pH values below the point of zero charge for goethite (i.e. $< 9.2$, Filius et al., 2000). This adsorption involves the formation of inner-sphere complexes via ligand exchange between the oxygen of FA carboxylate groups and the surface oxygen atoms coordinated to Fe at the goethite surface (Filius et al., 2003). Fourier transform infrared (FTIR) spectroscopy confirms the formation of this inner-sphere Fe-fulvate complex by virtue of a shift in the asymmetric carboxylate stretch vibration at pH 5 (Fu and Quan, 2006). Humic compounds obtained from various natural environments also complex strongly, and reversibly, with mononuclear Fe, exhibiting stability constants of $10^{21.0}$ to $10^{21.4}$ for Fe-humic complexes isolated from a river plume (Muller and Batchelli, 2011), with lower stability constants (i.e. $K = 10^{11.5}$ to $10^{14.0}$) observed for Fe-FA complexes obtained from soil (Pandeya, 1993).

Although the effects of low MW acids such as oxalate and citrate on DFOB mediated dissolution of goethite have been examined previously (Reichard et al., 2007a,b), the influence of the higher MW fulvic acid has not yet been explored despite the ubiquity of this humic material in soils and sediments. In this paper we report, for the first time, the results of batch experiments examining the dissolution of goethite in the presence of both Suwannee River fulvic acid (SRFA) and DFOB. The effects of SRFA presence and reagent addition
sequence were investigated at pH 6.5 to elucidate dissolution mechanisms. The aims of the study were to: (i) determine the effect of SRFA presence on goethite dissolution by DFOB; (ii) develop a mechanistic model of how SRFA influences DFOB function; (iii) characterise possible aqueous Fe-DFOB and Fe-SRFA complexes formed; (iv) propose an overall dissolution mechanism for the goethite-DFOB-SRFA system.

2. MATERIALS AND METHODS

2.1. Goethite synthesis and characterisation

Goethite was synthesised following the method of Schwertmann and Cornell (1991). Briefly, 180 mL of 5 M KOH (Fisher Chemicals, SLR) was rapidly added to 100 mL of 1 M Fe(NO$_3$)$_3$.9H$_2$O (BDH, AnalaR) in a 2 L plastic beaker with constant stirring for 10 min. The suspension was brought to 2 L with ultrapure water (18 MΩ-cm, Milli-Q Millipore) and transferred to five 500 mL amber wide-mouth Nalgene HDPE screw top bottles then aged for 24 h at 70 °C (Dubbin and Ander, 2003). The precipitate was washed with ultrapure water through a Büchner funnel into a Büchner flask using Whatman no. 40 filter paper, which was replaced after every 250 mL of suspension to prevent clogging. The precipitate was then allowed to air-dry at 21 °C.

The hydroxy Fe precipitates were confirmed as goethite (α-FeOOH) by powder X-ray diffraction (XRD) analyses on an Enraf-Nonius PSD 120, equipped with an INEL 120° curved position sensitive detector utilising Cu Kα$_1$ radiation (45 kV and 45 mV) at 25 °C. N$_2$ multipoint BET surface area measurements were carried out using a Micrometrics Gemini III 2375 instrument. Samples were allowed to de-gas with N$_2$ at 100 °C for 24 h prior to surface
area determination. A kaolinite standard (15.9 ± 0.8 m²/g) was analysed alongside the
goethite samples to monitor accuracy.

2.2. Batch dissolution experiments

Stock solutions of: (i) DFOB obtained as the mesylate salt
\[\text{[(C}_{25}\text{H}_{46}\text{N}_{5}\text{O}_{8}\text{NH}_3}^-\text{(CH}_3\text{SO}_3^-)], \text{MW 656 g mol}^{-1}\} \text{ (Sigma-Aldrich); (ii) SRFA purchased from}
\text{the International Humic Substance Society [IHSS, Sample 1S101F, MW 1360 g mol}^{-1}\text{ (Chin}
\text{et al., 1994)); and (iii) synthetic goethite (α-FeOOH) were prepared in a combined}
buffer/electrolyte (MOPS/NaNO₃) solution for subsequent use in the batch dissolution
experiments. Both DFOB and SRFA were used as received to prepare a 500 µM stock
solution of DFOB (0.823 g DFOB dissolved in 250 mL MOPS/NaNO₃ solution) and a 65 mg
C L⁻¹ stock solution of SRFA (0.0624 g SRFA dissolved in 500 mL MOPS/NaNO₃ solution).
The goethite stock suspension was prepared to a concentration of 1256 mg L⁻¹ (3.14 g
goethite in 2500 mL MOPS/NaNO₃ solution). The combined MOPS/NaNO₃ solution
consisted of 1 mM 3-(N-morpholino) propanesulfonic acid (MOPS), a non-complexing
buffer (Electran VWR BDH PRO LAB molecular biology grade; pH range 6.5 – 7.9; \(\text{pK}_a\)
7.2), and 10 mM NaNO₃ (BDH Analar). The pH of the MOPS/NaNO₃ solution was
increased from pH 4.5 to 6.5 with the drop-wise addition of 0.1 M NaOH (BDH ARISTAR),
continuously monitored with a HANNA Instruments pH meter calibrated at two points (pH
4.01 and 7.01). The pH of the goethite suspensions, and DFOB and SRFA solutions, were
within the required range therefore no adjustment was required. Solutions and suspensions
were stored in amber HDPE wide-mouth screw top bottles to protect from photo-induced
reactions and stored at 4 °C to restrict microbial growth. All glassware and plasticware was
washed thoroughly with phosphate-free detergent (Decon 90) then rinsed several times with ultra pure water. Fig. 3 shows the reagents, addition sequences, and reaction times for each of the ten batch experiments. For batch experiments 1 through 8 (carried out in duplicate) 90 mL of goethite suspension was dispensed into each of eight 250 mL amber HDPE bottles. One of these eight bottles contained goethite alone (system 8), while a further two bottles without goethite served as procedural blanks to check for adsorption of DFOB (system 9) and SRFA (system 10) onto container walls. Subsequently, 9 mL of DFOB stock solution or 30 mL of SRFA stock solution were added to the bottles (with the exception of systems 3 and 5) as indicated in Fig. 3. The DFOB-SRFA complex was equilibrated for 30 minutes before addition to the goethite suspension (system 6). All batches were brought to a total volume of 129 mL with MOPS/NaNO₃ and left to equilibrate for 24 h at 25 °C on an orbital shaker (Orbital Incubator SI50) at 100 rpm. Following the initial 24 h contact, further reagents were added as indicated in Fig. 3, brought to final volumes of 168 mL, then placed on the orbital shaker for the duration of the reaction. In systems 3 and 5 we added DFOB and SRFA 4 h before the subsequent addition of, respectively, SRFA and DFOB, to more fully explore the effect of DFOB and SRFA addition sequence. A 4 hour reaction time was chosen because this duration had been reported as the optimal reaction period to achieve ligand adsorption without significant dissolution (Cocozza et al., 2002). The concentration of DFOB, where present, was 270 µM in all batch experiments. The pH of the suspensions in the 250 mL bottles was measured before and after the initial 24 h period, and at the end of the 330 h reaction. In all cases the pH was maintained at 6.5 and did not need further adjusting. Maintaining pH at 6.5 ensured that proton promoted dissolution was negligible. Changes in H⁺ activity may also influence ligand-controlled goethite dissolution by modifying the concentrations and speciation of
adsorbed ligands (Reichard et al., 2007b). Subsamples of the suspensions were obtained at intervals throughout the 330 h reaction, then filtered through 25 mm cellulose acetate filters (pore size 0.2 µm) followed by filtration through 25 mm nitrocellulose membrane filters (pore size 0.025 µm) into clear polythene screw cap tubes.

2.3. Analysis of supernatant solutions

Five mL portions of the filtrates were acidified with 100 µL 70% HNO₃ (Fisher Scientific) to prevent precipitation of Fe hydroxide then stored at 4 °C. These solutions were analysed for Fe using inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (VARIAN VISTA PRO Program ICP Expert version 4.1.0; emission line 259.94 nm; detection limit 89 nmol Fe L⁻¹). Aqueous SRFA and DFOB were quantified by UV-Vis spectroscopy (section 2.5). Total aqueous organic carbon (TOC) was determined by wet combustion with a Shimadzu 5000 TOC analyser after acidification of the filtrate with 10 µL concentrated HCl (BDH ARISTAR). To test the reliability of SRFA quantification by UV-Vis spectroscopy (Gan et al., 2007; Ghabbour and Davies, 2009), aqueous SRFA concentrations were also determined by TOC analysis, subtracting from the total organic C, that C assigned to DFOB as determined by chelometric UV-Vis spectroscopy analysis (section 2.5). Statistical significance among aqueous Fe, DFOB and SRFA concentrations for all batches was determined by applying the unpaired two-tailed Student's 𝑡-test with a level of significance of 𝑝 = 0.05. The precipitate retained on each membrane filter following filtration was air-dried at room temperature, placed in an air tight container and preserved for subsequent observation by scanning electron microscopy (SEM), atomic force microscopy (AFM) and FTIR analysis, described below.
2.4. FTIR spectroscopy

Synthetic goethite, untreated SRFA and DFOB, and aqueous complexes of SRFA and DFOB prepared in several mole ratios (2:1 Fe$^{3+}$-DFOB, 5:1 Fe$^{3+}$-SRFA, 1:1 DFOB-SRFA, and 5:1:1 Fe$^{3+}$-DFOB-SRFA) were analysed by FTIR. Iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O) was used to prepare the Fe$^{3+}$-complexes. Solid samples for FTIR analysis were obtained from the acidified aqueous complexes by concentrating the solutes through freeze drying (Triad LABCONCO with a JAVAC JL-10 high vacuum pump) to minimise infrared absorption by water and improve peak/band resolution. All samples, including the air-dried residues from filtration, were prepared for FTIR analysis using the KBr pellet technique (Prasad et al., 2006), mixing ~1 mg of sample with 100–200 mg spectroscopy grade KBr (Merck, IR spectroscopy, Uvasol®). When not in use, the pellets were stored in a desiccator to minimise uptake of water. All FTIR data were collected over 200–4000 cm$^{-1}$ on a Perkin Elmer Spectrum One FTIR spectrometer with dedicated spectrum handling software (version 5.0.1). The spectra have a resolution of 4 cm$^{-1}$ and are the aggregate of 128 scans.

2.5. SRFA and DFOB quantification

Filtrate SRFA was quantified by first obtaining a UV-Vis scan (220-900 nm) of a standard aqueous SRFA solution (31.2 mg SRFA L$^{-1}$) to obtain the $\lambda_{\text{max}}$ (254 nm). A series of aqueous SRFA solutions of varying concentration were then prepared to construct the calibration curve. Aqueous SRFA from each batch dissolution experiment was then determined by placing 1 mL filtrate in micro cuvettes of 10 mm path length and measuring UV absorption at 254 nm (Qu et al., 2003; Tatár et al, 2004). Absorbance readings were obtained on a Shimadzu UV-1800 spectrophotometer fitted with tungsten iodine (visible) and
deuterium (UV) lamps. An aliquot of acidified MOPS/NaNO$_3$ was used to base correct the UV-Vis spectrophotometer before analysis of batch solutions.

Siderophore concentrations in the filtrates from the adsorption experiments were determined following the chelometric method (Cocozza et al., 2002; Cheah et al., 2003).

Spectrophotometric measurements of the Fe-DFOB complex were obtained at 467 nm within 1 h after filtration. Filtrates and standards were acidified to pH 1.5 to 1.7 with 8 µL 70% HClO$_4$ (BDH ARISTAR). We then added 170 µL of 15 mM Fe(ClO$_4$)$_3$ to each filtrate sample to give an Fe concentration in excess of that needed to complex all DFOB. Analogous siderophore-free blank solutions containing only MOPS buffer, background electrolyte and added Fe were likewise acidified to pH 1.5 to 1.7. Subtraction of absorbance for the blank solution from that for the sample filtrates yielded the net absorbance, which we attribute to siderophore not adsorbed. The DFOB surface excess (µmol g$^{-1}$) was determined by dividing the siderophore concentration loss (i.e. 270 µM minus DFOB concentration in the filtrate) by the goethite concentration. DFOB quantification in system 9 (i.e. DFOB without goethite) served as a validation step to account for any DFOB sorbed to container walls and filters.

UV-Vis spectra were obtained for DFOB, Fe(ClO$_4$)$_3$, SRFA, Fe$^{3+}$-DFOB, Fe$^{3+}$-SRFA, DFOB-SRFA and Fe-DFOB-SRFA standard solutions prepared in a MOPS/NaNO$_3$ matrix and compared to the spectra of the batch filtrate solutions. Furthermore, the spectrum of a MOPS/NaNO$_3$ solution was compared to that of deionized water to ensure that MOPS/NaNO$_3$ peaks did not overlap those from Fe-DFOB.

2.6. SEM and AFM imaging

Goethite morphology was determined before and after reaction with SRFA and DFOB. Powdered goethite samples were fixed to Al stubs then coated with Au-Pd prior to
analysis on a Zeiss Gemini Ultra Plus SEM operating at 5.0 kV and a spot size of 20.00 µm
over a range of magnifications to observe gross particle morphology. AFM was used to
determine the surface relief of the goethite crystals. The analysis was conducted using an
Asylum MFP-3D-SA (Santa Barbara, USA) instrument in AC mode. The prepared film
samples (1 cm²) were placed on glass slides and scanned in air over a 10 × 10 µm² area using
an Olympus AC240TS tip (spring constant 2 N m⁻¹). Surface roughness, amplitude and height
channels were monitored and analysed using IGOR PRO software.

3. RESULTS

3.1. Characterisation of goethite

The addition of 5 M KOH to 1 M Fe(NO₃)₃·9H₂O produced a brownish-yellow
precipitate of Munsell colour 10YR 6/8. The precipitates were confirmed as goethite (α-
FeOOH) by comparing their powder X-ray diffraction patterns with those reported in the
International Centre for Diffraction Data® Files (ICDD Files 1081-464). All the peaks
produced by the precipitates related to the structure of goethite; the absence of extraneous
peaks indicated that no other phases were present at detectable levels.

Analysis of goethite morphology by SEM showed the crystals to be lathed shaped as
observed previously (Cornell et al., 1974; Kosmulski et al., 2004). The fractured appearance
of some crystals we attribute to desiccation and water loss under high vacuum. The height of
the crystals obtained through AFM analysis was ~ 60 nm, while the N₂-BET surface area was
43 m² g⁻¹, slightly greater than that reported elsewhere (e.g. 35±3 m² g⁻¹; Kraemer et al.,
1999; 38 m² g⁻¹; Carrasco et al., 2007). Sorbed SRFA imparts surface roughness to goethite
and disrupts its characteristic lath-shaped morphology.
3.2. Goethite dissolution

Iron release kinetics for goethite dissolution in the presence of DFOB and/or SRFA at 270 μM initial siderophore concentration are shown in Fig. 4. Soluble Fe is detected only for those systems containing both goethite and DFOB (i.e. systems 1–6). At reaction times > 50 h Fe release broadly followed zero-order kinetics, with Fe concentration depending linearly on time (Table 1). This linearity is commonly observed for far from equilibrium dissolution reactions (Sposito, 1994; Lasaga, 1998), where the slope of the regression line equation (Table 1, column 2) is equal to the zero-order rate coefficient. Generally, goethite suspensions containing both DFOB and SRFA (e.g. systems 4, 5, 6) show increased slopes of the linear fits and greater soluble Fe than those containing only DFOB (i.e. system 1). This observation corroborates the complementary work of Reichard et al. (2007a) on two-ligand systems, who reported increased goethite dissolution at pH 6 in the presence of 50 μM DFOB alongside 50 μM oxalate, malonate, succinate or fumarate. These workers observed that in the presence of 50 μM DFOB alone, goethite dissolution yielded ~ 5 μM Fe, but this increased to nearly 10 μM Fe with the addition of the above low molecular weight organic ligands. Furthermore, in our study, addition of SRFA prior to DFOB (i.e. systems 4 and 5) yielded greater slopes than for those systems where DFOB was introduced prior to SRFA (i.e. systems 2 and 3). Introduction of the DFOB-SRFA complex to the goethite suspension (system 6) gave rise to the greatest Fe release.

In dissolution reactions under far from equilibrium conditions, the zero-order rate coefficient is generally considered to be proportional to either: (i) the specific surface area or (ii) the mass of the dissolving solid (Lasaga, 1998). However, as the normalisation of dissolution rates with respect to surface area is not straightforward (Brantley and Chen,
1995), we express the dissolution rates with respect to mass of the goethite. Mass normalised rate coefficients (µmol g\(^{-1}\) h\(^{-1}\)) were therefore derived as the slope of the linear fit divided by the goethite mass, and these coefficients are presented in column 3 of Table 1. The mass-normalised dissolution rate coefficients are greatest for those systems containing SRFA, particularly where this humic material was introduced prior to DFOB. Interestingly, the simultaneous introduction of DFOB and SRFA as the DFOB-SRFA complex (system 6) yielded the greatest rate coefficient of all systems.

The mass-normalised dissolution rate reported by Cocozza et al. (2002) for the dissolution of goethite by DFOB at 25 °C (i.e. 0.135 µmol g\(^{-1}\) h\(^{-1}\)) is approximately one-half that reported here (i.e. 0.257 µmol g\(^{-1}\) h\(^{-1}\)). Some of this difference may arise from the slightly higher concentration of DFOB used in this study (i.e. 270 µM vs. 240 µM). However, most of this difference in dissolution rate can be attributed to variation in the nature of the goethite sample. Cornell and Schwertmann (2003), for example, cite the influence of goethite morphology and crystallinity as important determinants of dissolution rate. The goethite used in this study was prepared using a method broadly similar to that adopted by Cocozza et al. (2002), with the exception that these earlier workers incorporated a longer aging period yielding a goethite which, presumably, displayed greater long-range order than that used in the present study.

UV-Vis spectra for untreated batch filtrates are shown in Fig. 5. These spectra reveal two main regions of absorption: a broad, low peak at 400 – 500 nm which is assigned to Fe\(^{3+}\)-DFOB, and another peak at 236 nm which is due to the uncomplexed anionic DFOB species, HDFOB\(^{2-}\), whose three hydroxamate groups are deprotonated whilst the terminal amine remains protonated (Edwards et al., 2005). We disregard other causes for the peak at 236 nm as UV-Vis scans of reference solutions of SRFA, Fe(ClO\(_4\))\(_3\), MOPS/NaNO\(_3\), Fe-DFOB, and Fe-SRFA did not show any absorption in this region. Thus, the spectra in Fig. 5 indicate that
the untreated filtrates contain both complexed DFOB as Fe$^{3+}$-DFOB and uncomplexed DFOB.

The values of surface excess of DFOB on goethite at 25 °C, pH 6.5 and 270 μM initial siderophore concentration are given in Table 1 (column 4) for the six systems containing both goethite and DFOB. Although we measure surface excess at a single temperature (i.e. 25 °C) Cocozza et al. (2002) report no significant change in surface excess of DFOB on goethite over the temperature range 25 °C to 55 °C for a comparable system. However, the surface excess we calculate for our system 1 (i.e. 14.4 µmol g$^{-1}$) is nearly five times that observed by Cocozza et al. (2002) (i.e. 2.99 µmol g$^{-1}$) under comparable conditions. We again attribute this difference to variation in goethite synthesis procedure, with attendant variation in crystallite morphology and density of reactive surface OH groups (Cornell and Schwertmann, 2003).

A pseudo-first-order rate coefficient may be used to characterise the kinetics of ligand-promoted dissolution under far from equilibrium conditions as described by Stumm et al. (1987). This approach was applied by Cocozza et al. (2002) to demonstrate the temperature dependence of DFOB mediated goethite dissolution at 55 °C, and the lack of temperature dependence over the range 25 to 40 °C. For the present study, the coefficient (h$^{-1}$) was derived as the ratio of the mass-normalised dissolution rate coefficient to the DFOB surface excess. These values are presented in Table 1 (column 5) and are generally in line with that reported by Kraemer et al. (1999) (i.e. 0.01 h$^{-1}$). This broad congruence of pseudo-first-order rate coefficients implies that differences in dissolution rate depend principally on DFOB surface excess as influenced by reagent addition sequence.

3.3. FTIR spectra
The dominant FTIR vibrations and corresponding assignments for the Fe-free and Fe$^{3+}$-complexed standards are shown in Table 2. All FTIR absorption peaks produced by our synthetic goethite relate to the structure of goethite. The absence of extraneous peaks indicated that no other phases were present at detectable levels. The FTIR spectrum for our synthetic goethite (Fig. 6) has an absorption band at 640 cm$^{-1}$, representing the FeO$_6$ lattice vibrations (Prasad et al., 2006). Other prominent vibrations are the in-plane ($\delta$) and out-of-plane ($\gamma$) deformational (bending) modes of hydroxyls at 891 cm$^{-1}$ and 795 cm$^{-1}$, respectively (cf., Prasad et al. 2006). The broad absorption band located at 3132 cm$^{-1}$ is assigned to the hydroxyl stretch of surface OH, previously reported at 3100 – 3150 cm$^{-1}$ (Cornell and Schwertmann, 2003).

In the FTIR spectrum for DFOB the terminal N-H stretching vibrations occur at 3128 cm$^{-1}$ and 3325 cm$^{-1}$, while the vibrational stretching of the amide I band of the C=O group occurs at 1624 cm$^{-1}$ (Cozar et al., 2006; Siebner-Freibach et al., 2006). Another C=O absorption band at 1599 cm$^{-1}$ represents the hydroxamate C=O (cf., Edwards et al., 2005; Domagal-Goldman et al., 2009). An absorption band at 1537 cm$^{-1}$ arises from the superposition of N-H bending and C-N stretching vibrations in the amide II group (cf., Nightingale and Wagner, 1954) as well as O-H (hydroxamate) in-plane bending vibrations (Cozar et al., 2006). The band at 1480 cm$^{-1}$ is assigned to both the hydroxamate NOH bend and the C-N oxime (hydroxamate resonance structure) stretch corresponding to the 1470 cm$^{-1}$ band of Edwards et al. (2005) (Fig. 6). We also observed a band at 1386 cm$^{-1}$ arising from a combination of vibrational deformation modes in the hydroxamate group and terminal N (cf., 1379 cm$^{-1}$ Edwards et al., 2005). An additional band, at 1047 cm$^{-1}$, coincides with the hydroxamate N-O resonance of DFOB. However, this band is not due exclusively to DFOB as methanesulfonate, the counter-ion of the DFOB mesylate salt, also shows strong absorption at 1049 cm$^{-1}$ (Borer et al., 2009; Simanova et al., 2010).
The FTIR spectrum for SRFA (Fig. 6) displayed two prominent absorption bands, at 3425 cm\(^{-1}\) and 1720 cm\(^{-1}\), and these were assigned to the phenolic O-H and protonated carboxylic acid C=O vibrational stretching modes, respectively (cf., International Humic Substance Society, 2008). Other absorption bands at 1629 cm\(^{-1}\) and 1384 cm\(^{-1}\) represent, respectively, the deprotonated asymmetric and symmetric vibrational stretching of carboxylate C-O (cf., Fu and Quan, 2006; Hay and Myneni, 2007). The broad band at 1218 cm\(^{-1}\), assigned to the O-H phenolic stretch, was previously observed at 1217 cm\(^{-1}\) by Fu and Quan (2006).

Complexation between DFOB and Fe\(^{3+}\) yields a shift in the amide I band to 1622 cm\(^{-1}\) from 1624 cm\(^{-1}\) (Fig. 6) as reported by Edwards et al. (2005). The hydroxamate absorption bands at 1537 cm\(^{-1}\) and 1480 cm\(^{-1}\), as well as the absorption band at 1386 cm\(^{-1}\), assigned to the hydroxamate near the terminal N, also disappeared upon complexation of DFOB to Fe\(^{3+}\). The Fe\(^{3+}\)-DFOB complex gave rise to a new vibrational stretching mode at 1568 cm\(^{-1}\), assigned to hydroxamate C=N, and a shift of the existing 1047 cm\(^{-1}\) band to 1045 cm\(^{-1}\), assigned to hydroxamate N-O (Fig. 6) (Cozar et al., 2006). Upon coordination of hydroxamate oxygen to Fe\(^{3+}\), a new hydroxamate absorption band emerged at 1459 cm\(^{-1}\), previously reported at 1455 cm\(^{-1}\) by Borer et al. (2009), in a region where bands at 1537 cm\(^{-1}\) and 1480 cm\(^{-1}\) once appeared (Table 2). The Fe\(^{3+}\)-DFOB complex also gives rise to a band at 561 cm\(^{-1}\), reported previously at 555 cm\(^{-1}\) (Cozar et al., 2006), attributed to the Fe-O stretching vibration, but distinct from the Fe-O stretching of the goethite lattice. Additionally, a broad and intense peak at 3368 cm\(^{-1}\), accompanied by two small shoulders, we attribute to the dissociation of the hydroxamate hydroxyl groups following Fe\(^{3+}\) coordination.

Following complexation of Fe\(^{3+}\) with SRFA, the O-H band at 3425 cm\(^{-1}\) becomes broader, and shifts to 3410 cm\(^{-1}\) (Fig. 6). In contrast, the COOH and asymmetric C=O bands at 1720 cm\(^{-1}\) and 1629 cm\(^{-1}\), respectively, disappeared, whilst new, slightly lower intensity
bands appeared at 1687 cm\(^{-1}\) and 1631 cm\(^{-1}\). Meanwhile, the peak at 1384 cm\(^{-1}\) became sharper and more intense following Fe\(^{3+}\) complexation with SRFA (cf., Fu and Quan, 2006), indicating the complexation of carboxylate oxygen to Fe\(^{3+}\).

Our FTIR assignments for the DFOB-SRFA and Fe\(^{3+}\)-DFOB-SRFA complexes are based on comparison of the FTIR spectra for DFOB, SRFA, Fe\(^{3+}\)-DFOB, Fe\(^{3+}\)-SRFA, DFOB-SRFA and Fe\(^{3+}\)-DFOB-SRFA. Upon formation of the DFOB-SRFA complex, the SRFA phenolic absorption band at 3425 cm\(^{-1}\) becomes less intense and slightly broader, shifting to 3417 cm\(^{-1}\), while another phenolic band at 1216 cm\(^{-1}\) shifted to 1218 cm\(^{-1}\) (Fig. 6). The intensity of the prominent SRFA carboxylic C=O band at 1720 cm\(^{-1}\) decreased significantly and shifted to 1719 cm\(^{-1}\), whilst the asymmetric C=O band at 1629 cm\(^{-1}\) shifted to 1626 cm\(^{-1}\).

With respect to the DFOB, bands assigned to the terminal amines shifted from 3128 cm\(^{-1}\) and 3325 cm\(^{-1}\) to a single band at 2939 cm\(^{-1}\) of lower intensity.

Formation of the Fe\(^{3+}\)-DFOB-SRFA complex changed the FTIR spectra for both SRFA and DFOB (Fig. 6). The intensity of the SRFA carboxylic C=O band was reduced, shifting from 1720 to 1723 cm\(^{-1}\), while the SRFA symmetric C=O absorption band at 1384 cm\(^{-1}\) disappeared. The SRFA phenolic OH band at 1216 cm\(^{-1}\) remained largely as it was in the DFOB-SRFA complex, whilst the asymmetric stretching of the carboxylate C=O increased from 1629 cm\(^{-1}\) in the Fe-free complex to 1642 cm\(^{-1}\) in the Fe\(^{3+}\)-DFOB-SRFA complex. The phenolic OH band shifted from 3425 cm\(^{-1}\) for the Fe-free SRFA to 3437 cm\(^{-1}\) for the Fe\(^{3+}\)-DFOB-SRFA complex. The N-O resonance of the hydroxamate group decreased from 1047 cm\(^{-1}\) in DFOB to 1042 cm\(^{-1}\) in the Fe\(^{3+}\)-DFOB-SRFA complex and was accompanied by considerable peak sharpening. Furthermore, the Fe-O vibration at 561 cm\(^{-1}\) indicating complexation between Fe\(^{3+}\) and DFOB was observed at 542 cm\(^{-1}\) in the ternary complex (Fig. 6). Weak bands at 3010 cm\(^{-1}\) and 2954 cm\(^{-1}\) for the Fe\(^{3+}\)-DFOB-SRFA complex are likely due to the decrease in frequency of the N-H group of the terminal N in the
DFOB as a result of electrostatic interaction between the DFOB terminal amine and charged SRFA groups.

4. DISCUSSION

4.1. Sorption of SRFA and DFOB to goethite

Adsorption of organic matter to iron oxide surfaces occurs by electrostatic interactions, ligand exchange, hydrogen bonding and van der Waals interactions (Sposito, 1984). Coulombic attraction of organic solutes to metal oxides can be predicted through construction of a Schindler diagram, a banded rectangle in which the charge properties of the adsorptive and adsorbent are compared as a function of solution pH (Fig. 7) (Schindler, 1990). The bottom rectangle displays a horizontal line indicating the pH range over which adsorption is expected to occur based solely on charge. Adsorption occurring outside of this range implies the involvement of specific adsorption mechanisms. On the basis of the Schindler diagram depicted in Fig. 7a, adsorption of SRFA to goethite is predicted over pH ~ 3 to 9.

At pH 6.5 and an initial SRFA concentration of 11.6 mg C L$^{-1}$, the surface excess of SRFA on goethite was 0.33 mg m$^{-2}$. This value compares favourably with that reported by Filius et al. (2000) for fulvate adsorption to goethite at pH 7 (i.e. 0.3 mg FA g$^{-1}$) and also Weng et al. (2006) for their system at pH 5.5 (i.e. 0.4 mg FA g$^{-1}$). FTIR spectra for the goethite-SRFA surface association were too complex to derive useful molecular-level information concerning adsorption mechanisms. However, FTIR spectra for aqueous Fe$^{3+}$-SRFA species, when compared with spectra for several reference aqueous complexes (Fig. 6), revealed that Fe$^{3+}$ forms inner-sphere complexes with COOH and phenolic OH of SRFA,
consistent with that reported in previous studies (Fu and Quan, 2006; Hay and Myeni, 2007).

Furthermore, application of the charge distribution multi-site complexation (CD-MUSIC) model provides theoretical evidence that carboxylic groups of SRFA form inner-sphere complexes with Fe via the singly coordinated surface hydroxyls of goethite (i.e. those hydroxyls coordinated to a single Fe$^{3+}$ cation) (Weng et al., 2005; Weng et al., 2006). On the basis of these theoretical predictions and our experimental data, we propose that SRFA binds to the goethite surface via inner-sphere complexation as depicted in Fig. 8, corroborating the work of Filius et al. (2000), who observed inner-sphere adsorption of fulvic acid at pH below the PZC for goethite. Importantly, SRFA adsorption lowers the PZC of goethite and reduces positive surface charge in the vicinity of the adsorption site (Tipping and Cooke, 1982).

The Schindler diagram shown in Fig. 7b predicts that goethite can serve as an effective sorbent for DFOB only at pH ~ 8 to 9. However, for our systems at pH 6.5, we observe a surface excess of DFOB ranging from 14.4 to 26.5 μmol g$^{-1}$ (Table 1). Much of this DFOB will be adsorbed via inner-sphere surface complexes (Carrasco et al., 2007), however electrostatic factors may be significant in increasing overall uptake. The predicted electrostatic repulsion at pH 6.5 between DFOB ($pK_a \sim 8.6$) and the positively charged goethite surface (PZC = 9.2) can be minimised through orientation of the approaching siderophore such that the hydroxamate group furthest from the protonated amine makes first contact with the surface (Cocozza et al., 2002). More significantly, adsorption of the anionic SRFA reduces the positive surface charge of goethite near the site of adsorption (Tipping and Cooke, 1982), thus facilitating localised uptake of DFOB. Consistent with the predicted SRFA enhanced uptake of DFOB, our data show that those systems with both SRFA and DFOB give rise to greater DFOB surface excess than system 1, which contains only DFOB (Table 1).
4.2. Aqueous complexes

UV-Vis spectroscopic analysis confirmed the presence of the Fe\(^{3+}\)-DFOB complex in supernatant solutions from batch dissolution experiments (Fig. 5). The emergence of FTIR absorption bands at 1459 cm\(^{-1}\) and 561 cm\(^{-1}\), assigned to Fe-O (Table 2; Fig. 6), following formation of the Fe\(^{3+}\)-DFOB complex provides evidence for presence of the Fe-hydroxamate bond as depicted in Fig. 1b. These observations are consistent with predictions based on the high affinity of desferrioxamine B for the Fe\(^{3+}\) cation (K = 10\(^{31}\)) (Kraemer, 2004).

The absence of both soluble Fe and the Fe\(^{3+}\)-SRFA species in the supernatant solutions of system 7 indicates that goethite dissolution does not occur at detectable levels in the presence of SRFA alone at pH 6.5 (Fig. 4). However, FTIR analysis of model compounds reveals the diagnostic absorption bands that indicate presence of the Fe\(^{3+}\)-SRFA complex, a species that may well form following the liberation of Fe\(^{3+}\) by DFOB. The most significant FTIR band arising from the complexation of SRFA with Fe is due to changes in the carboxylate C=O vibration, appearing at 1687 cm\(^{-1}\) in Fe\(^{3+}\)-SRFA and 1720 cm\(^{-1}\) in Fe-free SRFA. Fu and Quan (2006) observed similar changes in C=O vibrations when FA was sorbed to haematite. The other functional group indicative of Fe\(^{3+}\)-SRFA bonding, the phenolic OH, changes from 3425 cm\(^{-1}\) in the uncomplexed SRFA to 3410 cm\(^{-1}\) for Fe\(^{3+}\)-SRFA (Table 2).

Localisation of Fe within the ternary Fe-DFOB-SRFA complex can help to reveal the mechanisms of goethite dissolution when both organic ligands are present. The FTIR absorption band most diagnostic of Fe complexation by SRFA arises from the carboxylate C=O vibration which, when complexed to Fe, decreases from 1720 cm\(^{-1}\) to 1687 cm\(^{-1}\). In the ternary complex this vibration occurs at 1723 cm\(^{-1}\) (Table 2), broadly similar to that of the Fe-free SRFA. Furthermore, we observe the main band representing the Fe\(^{3+}\)-DFOB complex, the Fe-O vibration, is also present for the Fe-DFOB-SRFA complex, although
occurring at the somewhat lower frequency of 542 cm\(^{-1}\). On the basis of these spectroscopic observations we infer that Fe in the ternary complex is bound only to the hydroxamate groups of DFOB. Thus, in the presence of both DFOB and SRFA, dissolved Fe\(^{3+}\) is complexed by DFOB rather than SRFA, consistent with our observations, and as predicted by the much higher affinity of Fe\(^{3+}\) for DFOB than for SRFA at pH 6.5 (Pandeya, 1993; Kraemer, 2004; Muller and Batchelli, 2011). The FTIR spectrum for Fe-DFOB-SRFA also shows notable increases in wavenumber for SRFA phenolic OH (3437 cm\(^{-1}\)) and C=O (1642 cm\(^{-1}\)), compared to their uncomplexed form (Table 2). However, we believe these wavenumber shifts are not due to Fe complexation by SRFA but rather to ring strain caused by a change in SRFA conformation to accommodate the DFOB molecule as the Fe-O complex forms (Sharma, 2007).

FTIR data show that SRFA and DFOB combine to form intimate associations in aqueous solution. Specifically, bonding between the SRFA phenolic OH and the residual positive charge on the DFOB terminal NH\(_3\) group yields a significant wavenumber change for these groups, shifting the uncomplexed SRFA phenolic OH from 3425 cm\(^{-1}\) to 3417 cm\(^{-1}\) in the DFOB-SRFA complex (Table 2). Curiously, the SRFA phenolic OH appears to dominate these associations, despite the greater population of carboxyl groups within this humic material, with reports of carboxyl:phenol molar ratios varying from 3:2 (Alvarez-Puebla et al., 2006) to 4:1 (Ritchie and Perdue, 2003). The FTIR bands for the DFOB terminal NH\(_3\) group vibrations display even greater wavenumber shifts, from 3128 cm\(^{-1}\) and 3325 cm\(^{-1}\) in the uncomplexed siderophore to a single absorption peak at 2939 cm\(^{-1}\) in the DFOB-SRFA complex.

### 4.3. Influence of DFOB and SRFA on goethite dissolution
DFOB adsorbs to goethite principally via inner-sphere surface complexes (Carrasco et al., 2007), the necessary first step in ligand-controlled dissolution. The rate law for ligand-controlled dissolution predicts that the mass-normalised dissolution rate of goethite, $R_{\text{DFOB}}$, will be proportional to the DFOB surface excess, $n_{\text{DFOB}}$: 

$$R_{\text{DFOB}} = k_{\text{DFOB}} n_{\text{DFOB}}$$

where $k_{\text{DFOB}}$ is a pseudo first-order rate coefficient. The dissolution of goethite by siderophores obeys this rate law under many experimental conditions, even in the presence of low MW organic ligands such as oxalate (Cheah et al., 2003). Our values for $k_{\text{DFOB}}$ show little variation irrespective of treatment ($0.012 – 0.020 \text{ h}^{-1}$) (Table 1, column 5) and are broadly in line with that reported by Kraemer et al. (1999) (i.e. $0.01 \text{ h}^{-1}$). However, the pseudo first-order rate coefficient for dissolution of goethite by DFO-D1, the acetyl derivative of DFOB, increases to $0.05 \text{ h}^{-1}$ (Kraemer et al., 1999) while that for a simple monohydroxamate ligand, acetohydroxamic acid, was calculated as $0.073 \text{ h}^{-1}$ (Holmén and Casey, 1998).

In the present study, Fe release from goethite increased with the addition of SRFA, particularly where SRFA is added prior to DFOB (systems 4 and 5), and further still when SRFA is introduced as the DFOB-SRFA complex (system 6) (Fig. 4). A quantitative assessment of the effect of SRFA presence on goethite dissolution can obtained through comparison of the mass-normalised zero-order rate coefficients (Table 1, column 3). The rate coefficients for systems 4 ($0.364 \mu\text{mol g}^{-1} \text{ h}^{-1}$) and 5 ($0.412 \mu\text{mol g}^{-1} \text{ h}^{-1}$) are 40 to 60% larger than that for system 1 ($0.257 \mu\text{mol g}^{-1} \text{ h}^{-1}$), while the coefficient for system 6 ($0.440 \mu\text{mol g}^{-1} \text{ h}^{-1}$) is nearly 70% larger than for the SRFA-free system.
Despite the positive influence of SRFA on goethite dissolution by means of increased adsorption of DFOB (compare DFOB surface excess for system 1 with that for systems 2–6; Table 1, column 4), the rate of Fe release does not correlate linearly with DFOB surface excess. This nonlinear relationship between DFOB adsorption and goethite dissolution may reflect changes in surface speciation of DFOB when SRFA is present. The SRFA induced reduction in positive surface charge enables greater electrostatic adsorption of DFOB as predicted by Tipping and Cooke (1982). However, as formation of a DFOB inner-sphere complex is the required first step in ligand-controlled dissolution of goethite, DFOB held non-specifically through Coulombic forces would not contribute to goethite dissolution. Furthermore, in the case of system 6, inner-sphere complexation of DFOB to goethite may be partly limited by the rate at which DFOB and SRFA decouple. Nevertheless, the effect of SRFA presence on the DFOB-goethite system has important implications for the microbial acquisition of Fe in soils and other humic rich environments. Data in Fig. 4 show that for nearly all systems the efficacy of DFOB is increased with SRFA presence. For example, at reaction times of 120 and 330 h, system 1 (with only DFOB) yields 34.7 and 70.3 μM Fe while system 6 (containing both DFOB and SRFA) yields 71.6 and 125.7 μM Fe, respectively (Fig. 4). Thus, the benefit to the microbe producing the siderophore is substantial, and this advantage is achieved with little or no energetic cost to the organism.

4.4. Mechanism of SRFA enhanced goethite dissolution

Various mechanisms have been proposed to explain the effect of low MW organic acids on goethite dissolution by DFOB. For example, in their examination of the oxalate-DFOB-goethite system at pH 5, Cheah et al. (2003) suggest that Fe solubilised from the goethite surface by oxalate is subsequently wrested from the Fe$^{3+}$-oxalate aqueous complex.
by DFOB. Given sufficient DFOB to complex soluble Fe, oxalate will thus be liberated to react once again with the goethite surface. Reichard et al. (2007a), also examining the oxalate-DFOB-goethite system, proposed a dissolution mechanism broadly similar to that of Cheah et al. (2003), except that the former workers identified two distinct pools of labile Fe, namely, (i) Fe$^{3+}$ present as a residuum of goethite synthesis and (ii) kinetically labile Fe$^{3+}$ coordinated to unshared hydroxyls. The mechanism we propose here for the dissolution of goethite in the presence of DFOB and the higher MW organic compound, SRFA, differs from those proposed for oxalate in that SRFA plays a largely indirect, though no less important role in increasing the efficacy of DFOB. Adsorbed SRFA reduces the net positive surface charge of goethite, thereby increasing DFOB uptake, and also, through formation of Fe complexes with fulvic carboxyl and phenol groups, increases the pool of labile surface Fe. Our model for goethite dissolution by DFOB in the presence of SRFA, illustrated in Fig. 9, is summarised below:

(i) surface Fe of goethite is coordinated to SRFA via carboxylic (GOE)Fe$^{3+}$-OOC(SRFA) or phenolic (GOE)Fe$^{3+}$-O(SRFA) functional groups through ligand exchange;

(ii) the Fe$^{3+}$-SRFA attachment destabilises Fe-O bonds at the goethite surface, leading to labilisation of Fe$^{3+}$;

(iii) adsorbed SRFA locally reduces the positive charge on the goethite surface, thereby enhancing DFOB$^+$ uptake;

(iv) protons are displaced from the hydroxamate groups of DFOB as these groups bind to the labile Fe$^{3+}$ via ligand exchange;
(vi) the Fe$^{3+}$-DFOB$^+$ complex is released to solution where it remains a free species or subsequently complexes with aqueous SRFA.

5. CONCLUSIONS

Our results show that dissolution of goethite by DFOB is enhanced considerably through the presence of FA, particularly when FA sorption precedes that of DFOB, or when the two organic compounds are sorbed simultaneously. Importantly, our batch dissolution experiments incorporating FA reveal a more complex picture of siderophore function than is portrayed in the current literature. This humic material is revealed as a catalyst for goethite dissolution, in the sense that FA enhances the efficacy of DFOB but is itself not directly involved in Fe solubilisation. This work shines important new light on the factors influencing Fe acquisition by microorganisms and plants in soils and sediments, environments in which humic materials are ubiquitous. The incorporation of natural organic matter such as FA into geochemical models of siderophore function is therefore essential to more accurately predict the geochemical cycling of Fe in these natural environments.

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Interactions of calcium and fulvic acid at the goethite-water interface.


Figure Captions

Figure 1. (a) Structural representation of desferrioxamine-B (DFOB). The terminating R group (i) is an amine (pK$_a$ = 10.9). The three hydroxyl groups (ii – iv) have pK$_a$ values of 9.8, 9.2 and 8.6, respectively (Colnaghi Simionato et al., 2006). The hydroxamate (oxime) group is shown along with the amide I (C=O) and amide II (N-H and C-N). Adapted from Whitnall and Richardson (2006). (b) Structure of DFOB bound to Fe$^{3+}$ as ferrioxamine B. DFOB is hexadentate, giving a complex with Fe$^{3+}$ comprised of three, five-membered rings. Adapted from Cramer et al. (1984).

Figure 2. Generalised depiction of the proposed molecular structure of FA based on the Temple-Northeastern-Birmingham (TNB) molecular modelling programme (Alvarez-Puebla et al. (2006), in accordance with the experimentally derived elemental composition, number and type of acidic groups, and molecular weight of FA.

Figure 3. Graphical representation showing the permutations of the batch dissolution of goethite with DFOB and SRFA as a function of reaction duration.

Figure 4. Iron release by goethite in the presence of only DFOB (system 1) and both DFOB and SRFA (systems 2 – 6), with permutations as described in Fig. 3. System 7 is a goethite-SRFA suspension; system 8 is a goethite suspension lacking any organic ligand. Systems 9 and 10 are solutions of DFOB and SRFA, respectively, and serve as controls. Initial siderophore concentration: 270 μM; solid concentration: 0.7 g L$^{-1}$; pH 6.5.
Figure 5. UV-Vis spectra of untreated filtrate solutions showing absorbance for uncomplexed DFOB (270 µM) near 236 nm and absorbance for the Fe-DFOB complex appearing as a low, broad peak at 400 – 500 nm.

Figure 6. FTIR spectra for synthetic goethite, DFOB, SRFA, Fe-DFOB, Fe-SRFA, DFOB-SRFA and Fe-DFOB-SRFA. Reference compounds have the following molar ratios:- Fe:DFOB (2:1), Fe:SRFA (5:1), DFOB:SRFA (1:1) and Fe:DFOB:SRFA (5:1:1). See Table 2 for peak assignments.

Figure 7. Schindler diagrams illustrating the charge properties of goethite and ionic SRFA and DFOB. The horizontal bar in the bottom rectangle indicates the pH range over which purely electrostatic adsorption mechanisms are possible.

Figure 8. Proposed adsorption mechanism for the goethite-SRFA complex, involving a chelate ring incorporating COO- and phenolic OH from SRFA.

Figure 9. Proposed mechanism of goethite dissolution in the presence of DFOB and SRFA.
Table 1. Linear regression equations, mass-normalised zero-order dissolution rate coefficients, surface excess values for DFOB, and pseudo-first-order rate coefficients for goethite dissolution at pH 6.5 and 25°C.

<table>
<thead>
<tr>
<th>System</th>
<th>Regression equation</th>
<th>Rate coefficient (µmol g(^{-1}) h(^{-1}))</th>
<th>DFOB surface excess (µmol g(^{-1}))</th>
<th>Pseudo-first-order rate coefficient (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Y = 0.180X + 11.90</td>
<td>0.257 ± 0.016</td>
<td>14.4</td>
<td>0.018</td>
</tr>
<tr>
<td>2</td>
<td>Y = 0.191X + 14.94</td>
<td>0.273 ± 0.009</td>
<td>19.0</td>
<td>0.014</td>
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<tr>
<td>3</td>
<td>Y = 0.188X + 10.00</td>
<td>0.268 ± 0.034</td>
<td>23.3</td>
<td>0.012</td>
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<tr>
<td>4</td>
<td>Y = 0.255X + 14.66</td>
<td>0.364 ± 0.014</td>
<td>18.3</td>
<td>0.020</td>
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<tr>
<td>5</td>
<td>Y = 0.289X + 14.08</td>
<td>0.412 ± 0.000</td>
<td>26.5</td>
<td>0.016</td>
</tr>
<tr>
<td>6</td>
<td>Y = 0.308X + 29.72</td>
<td>0.440 ± 0.070</td>
<td>22.8</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Initial DFOB concentration = 270 µM
Goethite concentration = 0.7 g L\(^{-1}\)
Y = soluble Fe (µM)
X = time (h)
Table 2. FTIR absorption bands (cm$^{-1}$) and their assignments for DFOB, synthetic goethite, SRFA and four complexes: Fe-DFOB, Fe-SRFA, DFOB-SRFA and Fe-DFOB-SRFA.

Assignments are based on Cornell and Schwertmann (2003); Edwards et al. (2005); Cozar et al. (2006); Prasad et al. (2006); and Borer et al. (2009). Vibration modes are designated as follows: $\nu$, stretching; $\delta$, deformation; s, symmetrical; as, asymmetric.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>DFOB</th>
<th>Goethite</th>
<th>SRFA</th>
<th>Fe-DFOB</th>
<th>Fe-SRFA</th>
<th>DFOB-SRFA</th>
<th>Fe-DFOB-SRFA</th>
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<tr>
<td>$\nu\text{C}=\text{O}$ amide I</td>
<td>1624</td>
<td>1662</td>
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<tr>
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<tr>
<td>$\nu\text{C}=\text{N}$ hydroxamate (resonance)</td>
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<td>1568</td>
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</tr>
<tr>
<td>$\delta\text{N-H}$, $\nu\text{C}=\text{N}$ amide II</td>
<td>1537</td>
<td>1537</td>
<td>1537</td>
<td>1537</td>
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</tr>
<tr>
<td>$\delta\text{NHO}$, $\nu\text{C}=\text{N}$, $\nu\text{C}=\text{N}$ hydroxamate X2, adjacent to hydroxamate</td>
<td>1480</td>
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<tr>
<td>$\nu\text{Fe-O}$ hydroxamate-iron</td>
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<tr>
<td>$\nu\text{OH}$ (phenolic)</td>
<td>3425</td>
<td>3410</td>
<td>3417</td>
<td>3437</td>
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<tr>
<td>$\nu\text{OH}$ (terminal N)</td>
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<td>3128</td>
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<tr>
<td>$\nu\text{C}=\text{O}$ carboxylic acid protonated</td>
<td>3325</td>
<td>3325</td>
<td>3325</td>
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<tr>
<td>$\nu\text{C}=\text{O}$ carboxylic acid deprotonated</td>
<td>1720</td>
<td>1687</td>
<td>1719</td>
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<tr>
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<tr>
<td>$\delta\text{OH}$ in-plane-hydroxyl</td>
<td>1218</td>
<td>1218</td>
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<tr>
<td>$\delta\text{OH}$ out-of-plane hydroxyl</td>
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<td>640</td>
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<tr>
<td>$\nu\text{FeO}_6$ lattice mode</td>
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</tbody>
</table>
Phenolic group: \((C_6H_5)OH, HO(H_5C_6)\)
Carboxylic acid group: COOH, HOOC
Figure 3
Click here to download high resolution image

The diagram illustrates the progression of systems over time, with each system labeled from 1 to 10. The time scale is marked from 0 to 330 hours. Each system is divided into segments indicating the presence or absence of different substances, as indicated by the legend:

- Goethite
- DFOB
- SRFA
- Goethite+DFOB
- Goethite+SRFA
- Goethite+DFOB+SRFA
- Goethite+DFOB-SRFA complex

The segments vary in shading and pattern to represent the presence or interaction of these substances within each system over time.
Figure 4
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Figure 5
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Figure 7
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(a)

SURFACE (GOETHITE)

SOLUTE (SRFA)

pH of solution (6.5)

H⁺  A⁻

pH 1 2 3 4 5 6 7 8 9 10 11 12 13 14

pKₐ SRFA (3.0)  PZC goethite (9.2)

(b)

SURFACE (GOETHITE)

SOLUTE (DFOB)

pH of solution (6.5)

DFOB⁺  DFOB²⁻

pH 1 2 3 4 5 6 7 8 9 10 11 12 13 14

pKₐ DFOB (8.6)

PZC goethite (9.2)
Section of SRFA molecule binding to goethite surface via Fe$^{3+}$
Figure 9
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Step 1. At pH 6.5, SRFA surface is negatively charged, and goethite surface is positively charged.

Step 2. Areas on the goethite surface become less positive in the vicinity of the SRFA molecule.

Step 3. The hydroxamate furthest from the protonated amine in the DFOB bonds to the less positive areas on the goethite surface.

Step 4. DFOB bonds with Fe$^{3+}$ on the goethite surface. The new Fe$^{3+}$-DFOB complex then detaches from the surface into solution and approaches other SRFA molecules.