

Supporting Information

to

Modelling the Kinetics of Fe(II) Oxidation in the Presence of Citrate and Salicylate in Aqueous Solutions at pH 6.0–8.0 and 25 °C

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S-1. Testing of the Validity of the Kinetic Analysis Methodology

The purpose of this test was to determine whether the $\text{Fe}^{\text{II}}\text{FZ}_3$ absorbance measured in this work is representative of the concentration of either the inorganic Fe(II) or the total Fe(II) (i.e., both inorganic and organic Fe(II)).

Previous studies ^{1,2} suggested that FZ only reacts with Fe(II) complexes disjunctively and that the dissociation of organically complexed Fe(II) is slow compared to the timescale of investigation. Under such conditions, the measured absorbance at 562 nm (of the $\text{Fe}^{\text{II}}\text{FZ}_3$ complex) is therefore representative of the concentration of inorganic Fe(II) species only. Santana-Casiano and co-workers ³ also assumed that FZ only measures inorganic Fe(II) in studies of the kinetics of Fe(II) oxidation in the presence of salicylate and phthalate.

Recently, Pham ⁴ has shown that FZ is capable of interacting directly with organic complexes of Fe(II) through formation of a ternary complex (i.e., an adjunctive pathway of $\text{Fe}^{\text{II}}\text{FZ}_3$ formation). The rate constant for complexation of $\text{Fe}^{\text{II}}\text{cit}^-$ by FZ is estimated to be $2.24 \times 10^9 \text{ M}^{-3}\text{s}^{-1}$ at pH 6.0 and $1.50 \times 10^9 \text{ M}^{-3}\text{s}^{-1}$ at pH 8.0 ⁴. Because the exchange kinetics is a function of incubation time between FZ and the Fe(II) complex, the FZ concentration, and the strength of the initial complex, it is quite possible that the extent of adjunctive interaction of FZ with the Fe(II) complex may have been relatively insignificant in these earlier studies (incubation time is not specified in Santana-Casiano et al. ³ study but it was ~ 2 s in Rose and Waite ² study). In addition, if the initial Fe(II) complex is present at a relatively low concentration (as is the case in studies with salicylate described in this work) it may not be possible to differentiate between the total Fe(II) and inorganic Fe(II).

In our previous study, ⁵ the absorbance of $\text{Fe}^{\text{II}}\text{FZ}_3$ measured colorimetrically at 562 nm using a Cary 50 Bio UV-visible spectrophotometer was demonstrated to be equivalent to total Fe(II). In this study, because different experimental conditions were examined, confirmation of entities represented by the

measured absorbance was made by comparing the Fe(II) concentrations measured using the FZ method and those measured using the FeLume method. [Details of the original FeLume method can be found in King ⁶ with additional insights presented in Rose and Waite ⁷]. Because the chemiluminescence signal measured using the FeLume method is representative of the total Fe(II) concentration, ⁷ if the data collected from this method is similar to that measured using the FZ method, then the absorbance at 562 nm from the FZ method can be presumed to be truly representative of the total Fe(II) concentration (i.e., the concentration of both inorganic and organic complexes).

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Figure S-1 clearly shows that the change in Fe(II) concentration measured using the FZ method is quite similar to that observed using the FeLume method in studies of the oxidative loss of 50 nM Fe(II) from solutions containing 50 μ M citrate at different pH. Therefore, the absorbance measured at 562 nm from the FZ method under the experimental conditions used in this study will be presumed to represent total Fe(II). Indeed, if 1 mM FZ was used (as in this study), then 99% of $\text{Fe}^{\text{II}}\text{cit}^-$ will be complexed by FZ within 2 s at pH 6.0 ($k_f = 2.24 \times 10^9 \text{ M}^{-3}\text{s}^{-1}$).

It should be noted that no measurement has been made in the presence of salicylate because the Fe(II)–salicylate complexes are present at extremely low concentrations (see section below) and thus differentiation between inorganic Fe(II) and total Fe(II) is not possible.

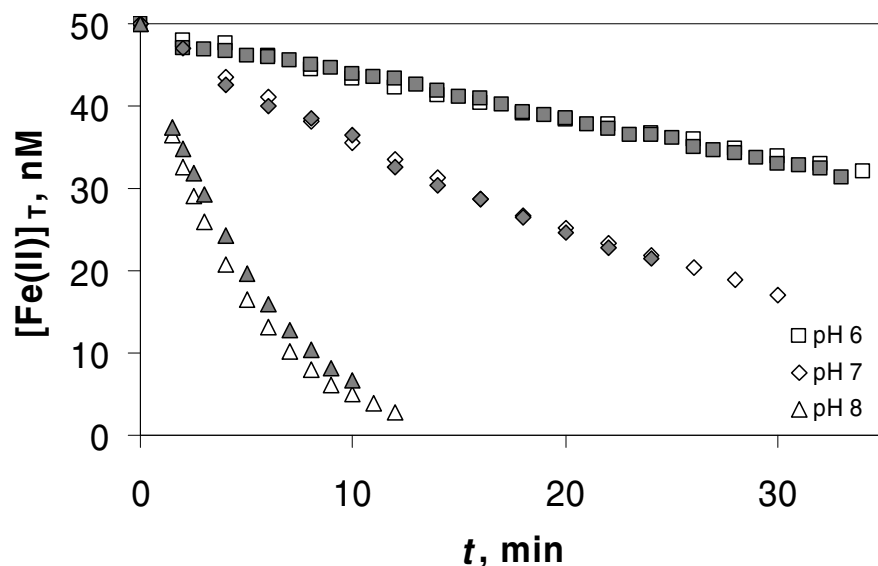


Figure S-1. Comparison between data measured using the FZ method (open symbols) and the FeLume method (filled symbols) for oxidation of 50 nM Fe(II) in the presence of 50 μ M citrate.

S-2. Speciation of Fe(II) in the Presence of Low Concentrations of Citrate and Salicylate

The speciation of Fe(II) in the presence of organic ligands was computed using the speciation package MINEQL⁺.⁸ A list of all equilibrium reactions considered in the speciation model is given in

[Table S-1](#) (in the presence of salicylate) and [Table S-2](#) (in the presence of citrate). The concentration of various important Fe(II) species (both organic and inorganic) at different combinations of $[\text{Fe(II)}]_0$ and $[\text{L}]_0$ is given in [Figure S-2](#).

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Table S-1. Thermodynamic Constants for Fe(II) Speciation in the Presence of Salicylate

no.	species	$\log K$, $I=0$, 25 °C	ref ^a
1	$H^+ + OH^- = H_2O$	14.0	1
2	$H^+ + CO_3^{2-} = HCO_3^-$	10.3	1
3	$2H^+ + CO_3^{2-} = H_2CO_3^*$	16.71	1
4	$H^+ + sal^{2-} = Hsal^-$	13.74	2
5	$2H^+ + sal^{2-} = H_2sal^0$	16.71	2
6	$NH_3 + H^+ = NH_4^+$	9.24	2
7	$H^+ + SO_4^{2-} = HSO_4^-$	1.99	2
8	$Fe^{2+} + H_2O = FeOH^+ + H^+$	-9.51	2
9	$Fe^{2+} + 2H_2O = Fe(OH)_2^0 + 2H^+$	-20.6	2
10	$Fe^{2+} + CO_3^{2-} = FeCO_3^0$	5.69	3
11	$Fe^{2+} + H^+ + CO_3^{2-} = FeHCO_3^+$	11.8	4
12	$Fe^{2+} + 2CO_3^{2-} = Fe(CO_3)_2^{2-}$	7.45	3
13	$Fe^{2+} + CO_3^{2-} + H_2O = Fe(OH)CO_3^- + H^+$	-4.03	3
14	$Fe^{2+} + Cl^- = FeCl^+$	0.30	3
15	$Fe^{2+} + SO_4^{2-} = FeSO_4^0$	2.42	3
16	$Fe^{2+} + sal^{2-} = Fesal^0$	7.4	2
17	$Fe^{2+} + 2sal^{2-} = Fesal_2^{2-}$	12.1	2
18	$Na^+ + CO_3^{2-} = NaCO_3^-$	1.27	3
19	$Na^+ + H^+ + CO_3^{2-} = NaHCO_3$	10.1	3
20	$Na^+ + SO_4^{2-} = NaSO_4^-$	1.06	3
21	$NH_4^+ + SO_4^{2-} = NH_4SO_4^-$	1.03	5

^a (1) Millero et al.,⁹ (2) Morel and Hering,¹⁰ (3) King,¹¹ (4) Millero and Hawke,¹² (5) Schecher and McAvoy.¹³

Table S-2. Thermodynamic Constants for Fe(II) Speciation in the Presence of Citrate

no.	species	$\log K,$ $I=0, 25\text{ }^{\circ}\text{C}$	ref ^a
1	$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	14.0	1
2	$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	10.3	1
3	$2\text{H}^+ + \text{CO}_3^{2-} = \text{H}_2\text{CO}_3^*$	16.7	1
4	$\text{H}^+ + \text{cit}^{3-} = \text{Hcit}^{2-}$	6.40	2
5	$2\text{H}^+ + \text{cit}^{3-} = \text{H}_2\text{cit}^-$	11.2	2
6	$3\text{H}^+ + \text{cit}^{3-} = \text{H}_3\text{cit}^0$	14.3	2
7	$\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$	9.24	2
8	$\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$	1.99	2
9	$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$	-9.51	2
10	$\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^0 + 2\text{H}^+$	-20.6	2
11	$\text{Fe}^{2+} + \text{CO}_3^{2-} = \text{FeCO}_3^0$	5.69	3
12	$\text{Fe}^{2+} + \text{H}^+ + \text{CO}_3^{2-} = \text{FeHCO}_3^+$	11.8	4
13	$\text{Fe}^{2+} + 2\text{CO}_3^{2-} = \text{Fe}(\text{CO}_3)_2^{2-}$	7.45	3
14	$\text{Fe}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} = \text{Fe}(\text{OH})\text{CO}_3^- + \text{H}^+$	-4.03	3
15	$\text{Fe}^{2+} + \text{Cl}^- = \text{FeCl}^+$	0.30	3
16	$\text{Fe}^{2+} + \text{SO}_4^{2-} = \text{FeSO}_4^0$	2.42	3
17	$\text{Fe}^{2+} + \text{cit}^{3-} = \text{Fecit}^-$	5.66	5 ^b
18	$\text{Fe}^{2+} + \text{H}^+ + \text{cit}^{3-} = \text{FeHcit}^0$	10.1	5 ^b
19	$\text{Fe}^{2+} + 2\text{cit}^{3-} = \text{Fecit}_2^{4-}$	7.00	5 ^b
20	$\text{Fe}^{2+} + \text{H}^+ + 2\text{cit}^{3-} = \text{FeHcit}_2^{3-}$	12.9	5 ^b
21	$\text{Fe}^{2+} + \text{H}_2\text{O} + 2\text{cit}^{3-} = \text{Fe}(\text{OH})\text{cit}_2^{5-}$	-2.18	5 ^b
22	$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	1.27	3
23	$\text{Na}^+ + \text{H}^+ + \text{CO}_3^- = \text{NaHCO}_3$	10.1	3
24	$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	1.06	3

25	$\text{Na}^+ + \text{cit}^{3-} = \text{Nacit}^{2-}$	1.03	6
26	$\text{Na}^+ + \text{H}^+ + \text{cit}^{3-} = \text{NaHcit}^-$	6.45	6
27	$2\text{Na}^+ + \text{cit}^{3-} = \text{Na}_2\text{cit}^-$	1.5	6
28	$\text{NH}_4^+ + \text{SO}_4^{2-} = \text{NH}_4\text{SO}_4^-$	1.03	6

^a (1) Millero et al.,⁹ (2) Morel and Hering,¹⁰ (3) King,¹¹ (4) Millero and Hawke,¹² (5) Konigsberger et al.,¹⁴ (6) Schecher and McAvoy.¹³ ^b Extrapolated to zero ionic strength using specific ion interaction theory (SIT),¹⁵ see Pham and Waite.⁵

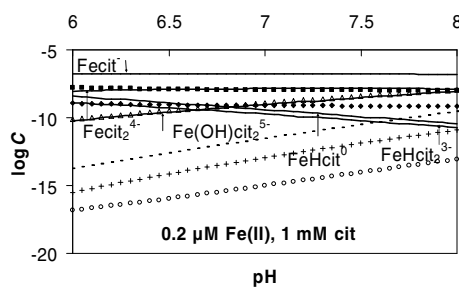
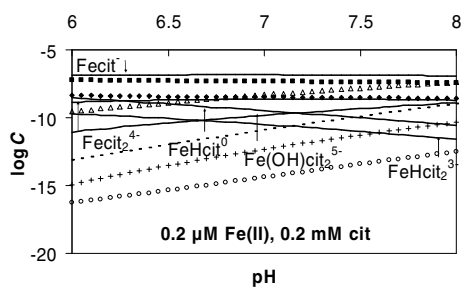
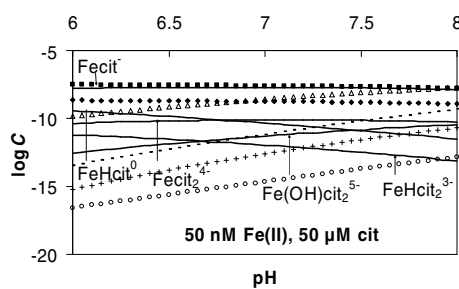
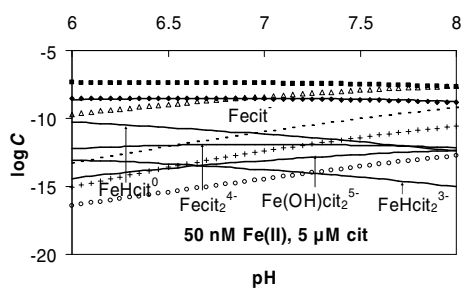
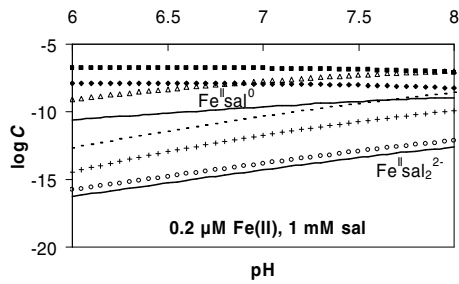
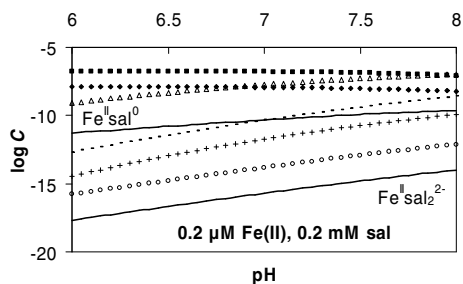
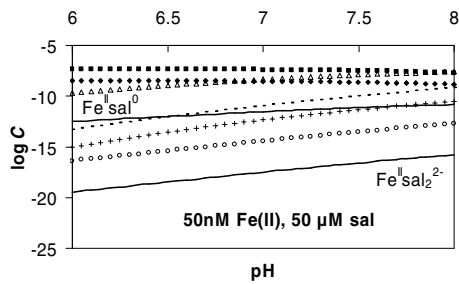
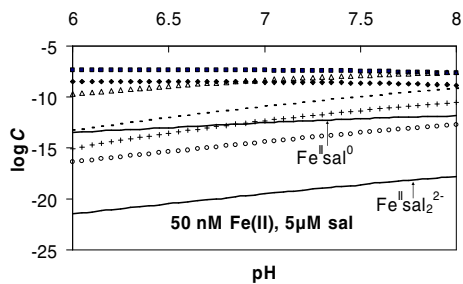


Figure S-2. Speciation of Fe(II) in the presence of low concentration of organic ligands. Symbols: (■) Fe^{2+} , (◆) FeCl^+ , (Δ) FeCO_3^0 , (-) Fe(OH)CO_3^- , (+) $\text{Fe(CO}_3)_2^{2-}$ and (\circ) Fe(OH)_2^0 . Solid lines are for organically complexed Fe(II). Minor Fe(II) species are not shown for clarity.

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Figure S-2 clearly shows that under the conditions investigated in this study, the major organically complexed Fe(II) species that are present are of monomeric form. In addition, while $\text{Fe}^{\text{II}}_{\text{cit}^-}$ becomes a dominant ferrous species at high concentrations of citrate, $\text{Fe}^{\text{II}}_{\text{sal}^0}$ dominates over other Fe(II) species even at low concentrations of salicylate.

S-3: Estimation of Reaction Rate Constants Using the Outer-sphere Complexation Model and the Linear Free Energy Relation Model

Estimation of k_7 , k_8 , k_{10} and k_{14} Using the Outer-sphere Complexation Model

The rate constants for reactions 7, 8, 10 and 14 can be crudely estimated by assuming that the kinetics of reaction between iron species with organic ligands and superoxide are controlled purely by the water loss kinetics at the metal coordination sphere (i.e., it is assumed that the outer-sphere complexation model¹⁶ is followed). The general formula for estimating the rate constant k_f of the reaction between Fe(II) and ligand L, according to this model¹⁶, is given below:

$$k_f = \sum K_{OS}(\text{Fe(II)}_i, L) \times k_{-w}(\text{Fe(II)}_i) \times \alpha_{\text{Fe(II)}_i} \quad \text{S-1}$$

where $K_{OS}(\text{Fe(II)}_i, L)$ is the stability constant of the outer-sphere complex formed between species Fe(II)_i and ligand L, $k_{-w}(\text{Fe(II)}_i)$ is the water loss rate of species Fe(II)_i and $\alpha_{\text{Fe(II)}_i}$ is the proportion of species Fe(II)_i in the total Fe(II) pool.

At pH 6.0, most Fe(II) is present as Fe^{2+} , thus $\alpha_{Fe(II)_i} \sim \alpha_{Fe^{2+}} = 1$ and eq S-1 becomes

$$k_f \sim K_{os}(Fe^{2+}, L) \times k_{-w}(Fe^{2+}) \quad S-2$$

In the case of salicylate, given that $k_{-w}(Fe^{2+}) \sim 1.0 \times 10^6 s^{-1}$ and $\log K_{os}(Fe^{2+}, sal^{2-}) = 1.13$ at $I = 0.1$, the effective rate constant of the reaction between Fe(II) and salicylate ion at pH 6.0 and $I = 0.1$ is estimated to be:

$$k_7^{eff} = k_f \sim (10^{1.13}) \times (1.0 \times 10^6) = 1.35 \times 10^7 \quad S-3$$

At pH = 6.0 and $I = 0.1$, $\frac{[sal^{2-}]}{[sal]_T} = 3.90 \times 10^{-8}$ and $\log^c K_{Fe^{II}sal^0} = 6.51$. Substituting these values into eqs 6 and 8 in the main article gives the estimated values of k_7 and k_8 in the case of salicylate at pH 6.0 and $I = 0.1$:

$$k_7 = k_7^{eff} \frac{[sal^{2-}]}{[sal]_T} \sim (1.35 \times 10^7)(3.90 \times 10^{-8}) = 0.53 \quad S-4$$

$$k_8 = \frac{k_7^{eff}}{^c K} = \frac{1.35 \times 10^7}{10^{6.51}} = 4.17 \quad S-5$$

Similarly, in the case of citrate, given that $\log K_{os}(Fe^{2+}, cit^{3-}) = 1.95$ at $I = 0.1$, the effective rate constant for the reaction between Fe(II) and citrate ion at pH 6.0 and $I = 0.1$ is estimated to be:

$$k_7^{eff} = k_f \sim (10^{1.95}) \times (1.0 \times 10^6) = 8.91 \times 10^7 \quad S-6$$

At pH 6.0 and $I = 0.1$, $\frac{[cit^{3-}]}{[cit]_T} = 0.50$ and $\log^c K_{Fe^{II}cit^-} = 4.32$ ¹⁴. Substituting these values into

eqs 6 and 8 in the main paper gives the estimated values of k_7 and k_8 in the case of citrate at pH 6.0 and $I = 0.1$:

$$k_7 = k_7^{eff} \frac{[cit^{3-}]}{[cit]_T} \sim (8.91 \times 10^7)(0.50) = 4.46 \times 10^7 \quad S-7$$

$$k_8 = \frac{k_7^{eff}}{^c K} = \frac{8.91 \times 10^7}{10^{4.32}} = 4.26 \times 10^3 \quad S-8$$

If the substitution of both salicylate and citrate ions does not significantly alter the rate of water loss from the metal coordination sphere (as has been observed with Febipy^{2+ 17}), then the rate constants of the reaction between $Fe^{II}sal^0$, $Fe^{III}sal^+$, $Fe^{II}cit^-$ and $Fe^{III}cit^0$ with O_2^- can be estimated directly from the water loss rate of Fe(II) and Fe(III) species (given that these water loss rate constants are already known). However, due to the variation of the reported water loss rates of Fe(II) (in the range from $1-4 \times 10^6 s^{-1}$ ¹⁰ for Fe^{2+}) and the uncertainty of the water loss rates of Fe(III) species¹⁸, the rate constants for the reaction between $Fe^{II}sal^0$, $Fe^{III}sal^+$ and $Fe^{II}cit^-$ with O_2^- at pH 6.0 are deduced from the pre-determined values of k_2 and k_4 ,¹⁹ and with the assumption that the difference between these rates is solely due to the difference in the magnitude of the outer-sphere stability constants. That is,

$$k_{Fe^{II}sal^0+O_2^-} = \frac{K_{os}(Fe^{II}sal^0, O_2^-)}{K_{os}(Fe(II), O_2^-)} \times k_2 = \frac{10^{-0.5}}{10^{0.31}} \times (1.0 \times 10^7) = 1.55 \times 10^6 \quad S-9$$

$$k_{Fe^{III}sal^++O_2^-} = \frac{K_{os}(Fe^{III}sal^+, O_2^-)}{K_{os}(Fe(OH)^{2+}, O_2^-)} \times k_4 = \frac{10^{-0.09}}{10^{0.31}} \times (1.5 \times 10^8) = 5.97 \times 10^7 \quad S-10$$

$$k_{Fe^{II}cit^{-}+O_2^{-}} = \frac{K_{OS}(Fe^{II}cit^{-}, O_2^{-})}{K_{OS}(Fe(II), O_2^{-})} \times k_2 = \frac{10^{-0.91}}{10^{0.31}} \times (1.0 \times 10^7) = 6.03 \times 10^5 \quad S-11$$

Because both $Fe^{II}sal^0$ and $Fe^{II}cit^{-}$ are the predominant complexes under the experimental conditions used in this study, $k_{10} = k_{Fe^{II}sal^0+O_2^{-}} = 1.55 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (in the case of salicylate) and $k_{10} = k_{Fe^{II}cit^{-}+O_2^{-}} = 6.03 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (in the case of citrate) would remain the same at any pH. On the other hand, as $Fe^{III}sal_2^{-}$ starts to dominate Fe(III)-complexes at higher pH, the assignment of $k_{14} = 6.03 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ may only be appropriate at pH 6.0 (where $Fe^{III}sal^{+}$ is present at approximately 13 times the concentration of $Fe^{III}sal_2^{-}$). In the model, we treat k_{14} as a fitting parameter (see Table 1, main article).

No attempt was made to estimate k_{14} in the case of citrate (even at low pH) due to the uncertainty of both the Fe(III)/citrate model^{14,20} and the nature of the oxidation products (i.e., competition for $Fe^{III}cit^0$ between O_2^{-} and citrate ion to form higher order complexes).

Estimation of k_9 and k_{11} Using the Linear Free Energy Relationship Model

If the reactions of $Fe^{II}sal^0$ and $Fe^{II}cit^{-}$ with O_2 and H_2O_2 were assumed to proceed via an outer-sphere electron transfer mechanism,²¹ then they would be expected to obey a linear free energy relation (LFER) and, as such, Marcus theory²² can be applied to estimate rate constants based on the free energy change of reactants.^{10,23} The general formula for the estimation of the second order rate constant of such reactions is given by:²⁴

$$k_{ox} = \frac{k_d}{1 + \frac{k_d}{K_d Z} \exp\left[\frac{\frac{\lambda}{4} \left(1 + \frac{\Delta G^o}{\lambda}\right)^2}{RT}\right]} \quad S-12$$

where $k_d = 10^{10} \text{ M}^{-1}\text{s}^{-1}$ is the diffusion controlled limit and the combined term $\frac{k_d}{K_d Z}$ is assigned a value of 0.1 (K_d is the equilibrium constant for the precursor complex and Z is the universal collision frequency factor).

The adjustable parameter λ is related to the energy required to reorganize the transition state and was determined to be 103 kJ/mole for inorganic Fe(II) complexes²⁵ and 135 kJ/mole for Fe(II)-NOM complexes.²⁶ In this study, for the purpose of crude estimation of the oxidation rate constants of $\text{Fe}^{\text{II}}\text{sal}^0$ and $\text{Fe}^{\text{II}}\text{cit}^-$ with O_2 and H_2O_2 , λ is assigned to be 103 kJ/mole given that the energy required for the transition state re-organization of these simple organic Fe(II) complexes is likely to be similar to that of inorganic Fe(II) complexes.

At standard state concentrations (1.0 M), standard free energy change (ΔG^0) for $\text{Fe}^{\text{II}}\text{L}$ oxidation to $\text{Fe}^{\text{III}}\text{L}$ via one electron reduction of oxygen to superoxide is given by:

$$\Delta G^0 = -F(E_{\text{O}_2 \rightarrow \text{O}_2^-}^0 - E_{\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}}^0) \quad \text{S-13}$$

where $E_{\text{O}_2 \rightarrow \text{O}_2^-}^0 = -0.16 \text{ V}$.²⁵

and that via one electron reduction of H_2O_2 to OH^\cdot is given by:

$$\Delta G^0 = -F(E_{\text{H}_2\text{O}_2 \rightarrow \text{OH}^\cdot}^0 - E_{\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}}^0) \quad \text{S-14}$$

where $E_{\text{H}_2\text{O}_2 \rightarrow \text{OH}^\cdot}^0 = 0.38 \text{ V}$.²⁵

The reduction potential $E_{\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}}^0$, on the other hand is estimated by applying the Nernst equation¹⁰ and given by⁵

$$E_{Fe^{III}L \rightarrow Fe^{II}L}^0 = E_{(Fe^{3+} \rightarrow Fe^{2+})}^0 - 0.059 \log_{10} \left(\frac{K_{Fe^{III}L}}{K_{Fe^{II}L}} \right) \quad S-15$$

where $E_{(Fe^{3+} \rightarrow Fe^{2+})}^0 = 0.77$ is the standard reduction potential of Fe^{3+} and K_i is the stability constant of the complex i .

For the estimation of rate constant of $Fe^{II}sal^0$ oxidation by O_2 , substituting $\frac{K_{Fe^{III}sal^+}}{K_{Fe^{II}sal^0}} = 10.2$ to

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eq [S-15](#) gives:

$$E_{Fe^{III}L \rightarrow Fe^{II}L}^0 = 0.77 - 0.059 \times 10.2 = 0.17 \quad S-16$$

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Substituting this value to eq [S-13](#), gives the standard free energy change (ΔG^0 , kJ mol^{-1}) for $Fe^{II}sal^0$ oxidation (to $Fe^{III}sal^+$) via one electron reduction of oxygen to superoxide,

$$\Delta G^0 = -\frac{96490 \times (-0.16 - 0.17)}{1000} = 31.8 \text{ kJ mol}^{-1} \quad S-17$$

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Substituting this value to eq [S-12](#), gives the oxidation rate constant of $Fe^{II}sal^0$ by O_2 of $k_9 = 1.92 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

Similarly, for the estimation of rate constant of $Fecit^-$ oxidation by O_2 , substituting

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$$\log \frac{K_{Fe^{III}cit^0}}{K_{Fe^{II}cit^-}} = 7.3 \text{ to eq } \text{S-15} \text{ gives:}$$

$$E_{Fe^{III}cit^0 \rightarrow Fe^{II}cit^-}^0 = 0.77 - 0.059 \times 7.3 = 0.34 \quad S-18$$

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Substituting this value to eq [S-13](#), gives the standard free energy change (ΔG^0 , kJ mol⁻¹) for Fe^{II}cit⁻ oxidation (to Fe^{III}cit⁰) via one electron reduction of oxygen to superoxide,

$$\Delta G^0 = -\frac{96490 \times (-0.16 - 0.34)}{1000} = 48.2 \text{ kJ mol}^{-1} \quad \text{S-19}$$

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Substituting this values to eq [S-12](#) gives $k_9 = k_{\text{Fe}^{\text{II}}\text{cit}^- + \text{O}_2} = 18.9 \text{ M}^{-1}\text{s}^{-1}$.

Similarly, the oxidation rate constant of Fe^{II}sal⁰ and Fe^{II}cit⁻ by H₂O₂ is estimated to be $k_{11} = 1.24 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $6.67 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ respectively.

S-4: Summary of the Kinetic Modelling of Inorganic Fe(II) Oxidation in Aqueous Solutions Over the pH Range 6.0–8.0

Details of the kinetic modeling of inorganic Fe(II) oxidation in aqueous solutions over the pH range 6.0–8.0 can be found in Pham and Waite.¹⁹ For the purpose of completeness of this article, the following summary provides a brief description of the model that is considered to be relevant to this paper.

Oxidation of low concentrations of Fe(II) over a range of circumneutral pH can be adequately described by the set of reactions given in [Table S-3](#) and the corresponding kinetic constants given in [Table S-4](#). In this model, the oxidation of Fe(II) by O₂ and O₂⁻ were found to be critically important at any pH and initial Fe(II) concentration considered. Oxidation of Fe(II) by H₂O₂ however only became critical at high pH and high Fe(II) concentrations or in the later stage of the oxidation process. Back reduction of Fe(III) by O₂⁻ was found to be important at low initial Fe(II) concentrations and high pH. Precipitation of Fe(III) on the other hand exerted a marked effect in the overall oxidation of Fe(II), particularly at high pH. Disproportionation of O₂⁻ was

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found to have minimal effect on the overall oxidation of Fe(II), despite the rapidity of this process at low pH.

Table S-3. Modeled Reactions for the Oxidation of Inorganic Fe(II).

No.	Reaction	Note
1	$\text{Fe(II)} + \text{O}_2 \rightarrow \text{Fe(III)} + \text{O}_2^-$	1
2	$\text{Fe(II)} + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2$	2
3	$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{OH}^\cdot + \text{OH}^-$	3
4	$\text{Fe(III)} + \text{O}_2^- \rightarrow \text{Fe(II)} + \text{O}_2$	2
5	$\text{Fe(III)} + \text{Fe}_\text{I} \rightarrow \text{AFO} + n\text{H}^+$	4
6	$\text{O}_2^- + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	5

(1) Fitting parameter, (2) Rush and Bielski,²⁷ (3) Gonzalez-Davila et al.,²⁸ (4) Pham et al.¹⁸ where Fe_I represents total inorganic Fe(III); AFO (amorphous ferric oxide) represents both polymeric and particulate forms of Fe(III), and (5) Zafiriou.²⁹

Table S-4. Kinetic Constants Used in the Inorganic Oxidation Model

pH	k_1 ($\text{M}^{-1}\text{s}^{-1}$)	$k_2 \times 10^7$ ($\text{M}^{-1}\text{s}^{-1}$)	$k_3 \times 10^3$ ($\text{M}^{-1}\text{s}^{-1}$)	$k_4 \times 10^8$ ($\text{M}^{-1}\text{s}^{-1}$)	$k_5 \times 10^6$ ($\text{M}^{-1}\text{s}^{-1}$)	$k_6 \times 10^5$ ($\text{M}^{-1}\text{s}^{-1}$)
6.0	0.11	1.0	0.62	1.5	0.32	60
6.5	0.17	1.0	1.72	1.5	1.0	19
7.0	0.39	1.0	4.79	1.5	3.4	6.0
7.5	1.24	1.0	13.3	1.5	5.0	1.9
8.0	8.81	1.0	37.2	1.5	16.1	0.6

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