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Influence of phosphate on the oxidation kinetics of nanomolar Fe(II) in aqueous solution at circumneutral pH

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Abstract

The oxygenation kinetics of nanomolar concentrations of Fe(II) in aqueous solution have been studied in the absence and presence of millimolar concentrations of phosphate over the pH range 6.0–7.8. At each phosphate concentration investigated, the overall oxidation rate constant varied linearly with pH, and increased with increasing phosphate concentration. A model based on equilibrium speciation of Fe(II) was found to satisfactorily explain the results obtained. From this model, the rate constants for oxygenation of the Fe(II)-phosphate species $\text{FeH}_2\text{PO}_4^+$, FeHPO_4 and FePO_4^- have been determined for the first time. FePO_4^- was found to be the most kinetically reactive species at circumneutral pH with an estimated oxygenation rate constant of $(2.2 \pm 0.2) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$. $\text{FeH}_2\text{PO}_4^+$ and FeHPO_4 were found to be less reactive with oxygen, with rate constants of $(3.2 \pm 2) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and $(1.2 \pm 0.8) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$, respectively.

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1. INTRODUCTION

Iron is an important micronutrient which is required for growth and metabolism of almost all living organisms (Sunda and Huntsman, 1995). In natural waters, iron exists in two primary oxidation states: Fe(II) and Fe(III). Despite being the second most abundant metal in the Earth's crust, the bioavailability of iron is often limited by the high insolubility of Fe(III). Furthermore, the more soluble form of iron, Fe(II), is rapidly oxidized to Fe(III) in oxygenated waters at circumneutral pH. The rate at which Fe(II) is oxidized to Fe(III) is therefore critical in determining the fate, forms and bioavailability of iron in many aqueous systems.

The effect of both inorganic and organic ligands on the rate of Fe(II) oxidation has been previously documented

(Stumm and Lee, 1961; Theis and Singer, 1974; Tamura et al., 1976; King, 1998; Rose and Waite, 2002; Santana-Casiano et al., 2005; Pham and Waite, 2008a). Amongst the various inorganic ligands that interact with Fe(II), phosphate has attracted considerable interest in part because phosphorus is also of great biological importance. As phosphate has a strong tendency to adsorb to iron oxide surfaces, the transformation of Fe(II) to Fe(III), with subsequent formation of iron oxides, is likely to be a critical determinant of both phosphate mobility and its availability to organisms in many natural systems including lakes and wetlands (Odum, 1988). Fe(III) has often also been used in wastewater treatment facilities to aid the removal of phosphorus and promote sedimentation. A range of processes under aerobic and anaerobic conditions may result in the simultaneous occurrence of Fe(II) and phosphate, with subsequent possible formation of the mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2$) (Wang and Waite, 2010) and/or oxidation of Fe(II) to Fe(III) with subsequent precipitation of either Fe(III) oxide or phosphate minerals. Finally, phosphate buffers, particularly phosphate buffered saline (PBS) solution (which contains approximately 10 mM phosphate),

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are commonly used in biological studies involving iron chemistry (Tamura et al., 1976; Reinke et al., 1995). The effect of the phosphate in these buffers on the kinetics of redox transformations of elements such as iron has received very little attention even though, in biological research, phosphate has been shown to stimulate the rate of iron loading into ferritin (Aitken-Rogers et al., 2004; Cutler et al., 2005), cause DNA damage as a result of its complexation by Fe(II) (Svoboda and Harms-Ringdahl, 2002), and promote redox cycling of iron in liver microsomes (Reinke et al., 1995).

Despite general agreement that the presence of phosphate enhances the rate of Fe(II) oxidation, discrepancies still exist between studies as to how and to what extent phosphate affects Fe(II) oxidation. The effect of phosphate on the kinetics of Fe(II) oxidation was first quantified by Cher and Davidson (1955), who indicated that the rate of Fe(II) oxidation in acidic medium could be described by the following rate law:

$$-\frac{d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}]P_{\text{O}_2}[\text{H}_2\text{PO}_4^-]^2 \quad (1)$$

where $k = 4.5 \pm 0.3 \text{ atm}^{-1} \text{ mol}^{-2} \text{ L}^2 \text{ h}^{-1}$ at 30°C .

Tamura et al. (1976) also found that the rate of oxidation of micromolar Fe(II) could be expressed as a function of the concentration of H_2PO_4^- .

$$-\frac{d(\text{Fe(II)})}{dt} = k[\text{Fe(II)}][\text{OH}^-][\text{O}_2][\text{H}_2\text{PO}_4^-]^n \quad (2)$$

where $k = 5.02 \times 10^9 \text{ M}^{-3} \text{ s}^{-1}$, $n = 1$ for $[\text{H}_2\text{PO}_4^-] < 0.1 \text{ M}$ and $k = 5.02 \times 10^{10} \text{ M}^{-4} \text{ s}^{-1}$, $n = 2$ for $[\text{H}_2\text{PO}_4^-] > 0.1 \text{ M}$.

Conversely, Mitra and Matthews (1985) concluded that HPO_4^{2-} was the sole phosphate species responsible for Fe(II) oxidation and estimated a second-order rate constant of $116.7 \text{ M}^{-1} \text{ min}^{-1}$ for the oxidation of FeHPO_4 by O_2 . Harris and Aisen (1973), however, ascribed this effect to the formation of a strong Fe(III) complex.

Varying explanations for the enhanced rate of Fe(II) oxidation resulting from the addition of phosphate imply that the mechanism of how phosphate affects Fe(II) oxidation is still uncertain. Thus, in this study, we reinvestigated the kinetics of Fe(II) oxidation in the presence of millimolar concentrations of phosphate at circumneutral pH. In comparison to previous studies where micromolar concentrations of Fe(II) were used (Cher and Davidson, 1955; Harris and Aisen, 1973; Tamura et al., 1976), nanomolar concentrations of Fe(II) were employed in this study to ensure that the effect of solid formation (both from Fe(II) and Fe(III) phosphate species) on the oxidation kinetics of Fe(II) was minimized. A speciation-based approach (King, 1998; Santana-Casiano et al., 2005) was used to examine the relative contributions of the key Fe(II)-phosphate species FePO_4^- , FeHPO_4 and $\text{FeH}_2\text{PO}_4^+$ to the overall oxidation kinetics of Fe(II) and to determine the second order oxygenation rate constants of these species. Although the existence of FePO_4^- has been considered in recent thermodynamic databases (e.g. Common Thermodynamic Database Project; <http://www.ctdp.org>), the role of FePO_4^- in the kinetics of Fe(II) oxidation has not been addressed prior to this study.

2. MATERIALS AND METHODS

2.1. Reagent preparation

Analytical grade reagents were used in all cases and purchased from Sigma–Aldrich unless otherwise stated. All solutions were prepared using $18 \text{ M}\Omega \text{ cm}$ ultrapure Milli-Q water (MQ) and stored in the dark at 4°C when not in use. All glassware and plasticware were soaked in 5% v/v HCl for several days and rinsed with MQ thoroughly before use.

A 1.0 mM Fe(II) stock solution was prepared monthly by dissolving an appropriate amount of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 0.2 M HCl. A working stock of 10 μM Fe(II) was prepared weekly by dilution of the 1.0 mM Fe(II) stock in 2 mM HCl solution. The acidity of Fe(II) stock solutions was sufficient to avoid significant oxidation of Fe(II) over relevant time-scales but was low enough to prevent significant pH change on addition to experimental solutions. A 1.0 M phosphate stock solution was prepared by dissolving an appropriate amount of NaH_2PO_4 in MQ.

Because Fe(II) oxidation can be strongly affected by solution pH, the pH of all solutions used was carefully controlled with an appropriate buffer (10 mM MES (SigmaUltra) for pH 6.0 and 6.5 and 10 mM Hepes (SigmaUltra) for pH 7.0, 7.5 and 7.8). Both MES and Hepes are non-complexing (Kandegedara and Rorabacher, 1999) and do not participate in the various reactions in which iron species are involved (King, 1998). To further confirm this, we performed an additional set of experiments (results not shown) where the oxidation of 200 nM Fe(II) was examined at different buffer concentrations (from 5 mM to 15 mM) at both pH 6.7 and 8.0. No significant difference in the oxidation kinetics of Fe(II) was found over this range of buffer concentrations. All buffer solutions initially contained 2.0 mM NaHCO_3 and 0.1 M NaCl. This buffer maintained solution pH within ± 0.02 pH units during the course of each experiment (Pham and Waite, 2008b). All buffer solutions were prepared 1 week prior to the commencement of each experiment in order to ensure that equilibrium was reached between the buffer solutions and the atmosphere. pH was measured using a HANNA 211 pH meter combined with a glass electrode and Ag/AgCl reference. NIST-traceable buffer solutions (pH 4.01, 7.01 and 10.01) were used to calibrate the electrode on the NBS scale. Any pH error due to ionic strength differences between the NIST standard buffers (pH 4.01, $I = 0.05$; pH 7.01, $I = 0.13$; and pH 10.01, $I = 0.05$) and experimental solutions ($I \sim 0.1$ in this work) is minor and can be neglected.

A 1.0 mM ferrozine (FZ) working solution was prepared by dissolving 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid monosodium salt hydrate in buffer solutions and pH was adjusted accordingly to the experimental conditions.

All experiments were performed under conditions in which light was minimized by wrapping the reaction vessel in dark cloth at $22 \pm 1^\circ\text{C}$.

2.2. Fe(II) analysis

Fe(II) concentrations were determined spectrophotometrically using the ferrozine method (Gibbs, 1976). In brief, FZ reacts extremely rapidly with Fe(II) (with rate constant $k = 3.1 \times 10^{11} \text{ M}^{-3} \text{ s}^{-1}$) (Thompson and Mottola, 1984; Lin and Kester, 1992) to form a stable, pink $\text{Fe}^{\text{II}}\text{FZ}_3$ complex (with stability constant $K = (7.2 \pm 0.3) \times 10^{15} \text{ M}^{-3}$) (Thompson and Mottola, 1984) with maximum absorbance at 562 nm and molar absorption coefficient of $\epsilon_{562\text{nm}} = 30,000 \text{ M}^{-1} \text{ cm}^{-1}$ (Stokey, 1970; Viollier et al., 2000). Furthermore, FZ does not bind Fe(III) to any significant extent (Pullin and Cabaniss, 2003) and therefore is suitable for quantifying the Fe(II) concentration in these experiments.

2.3. Fe(II) oxidation experiments

The oxidation of Fe(II) was examined by adding appropriate volumes of Fe(II) working stock solution to 50 mL of air-saturated buffer solutions that contained a known concentration of total phosphate ($[\text{PO}_4^{3-}]_T$). The dissolved O_2 concentration was calculated to be 266 μM under the experimental conditions at 22 °C and at 1 atm using the formula reported by Weiss (1970). The dissolved O_2 concentration was assumed to be constant over the course of Fe(II) oxidation experiments where nanomolar concentrations of Fe(II) were employed. pH was adjusted prior to the addition of iron. The initial Fe(II) concentrations ($[\text{Fe(II)}]_0$) were 200 nM and 50 nM and $[\text{PO}_4^{3-}]_T$ ranged from 0 mM to 10 mM.

The reaction solution and 1.0 mM FZ solution were drawn into a mixing tee at the same rate using a peristaltic pump and then passed through a 1.0 m pathlength spectrophotometric cell (LWCC Type II, World Precision Instruments). The concentration of the resulting $\text{Fe}^{\text{II}}\text{FZ}_3$ complex was determined colorimetrically at 562 nm using an Ocean Optics spectrophotometry system (Pham and Waite, 2008b). A reference wavelength of 690 nm was employed to account for any drift in the background absorbance signal due to fluctuations in lamp intensity. The spectrophotometer was zeroed for each experiment using a control solution (to which no iron was added) to account for the absorbance of the background solution and FZ at 562 nm. It was verified that FZ is able to bind all inorganic Fe(II) in the experimental solutions, including Fe(II)-phosphate species (results not shown). As such, the absorbance measured at 562 nm is equivalent to the total concentration of Fe(II), both in the absence and presence of phosphate. In addition, although limitations of the ferrozine method for quantitative assays of mineral systems for Fe(II) and total iron have been reported (Stucki, 1981; Stucki and Anderson, 1981; Amonette and Templeton, 1998; Anastacio et al., 2008), the effect of photochemical reduction of any Fe(III)-ferrozine complex that could potentially form under the current experimental conditions has been demonstrated to be negligible elsewhere (Pullin and Cabaniss, 2003) and verified in this work (results not shown).

Calibration curves were developed at each pH and phosphate concentration examined based on the absorbance

measured at 562 nm when different concentrations of Fe(II) (25, 50, 100, 200, and 400 nM) were added to buffer solutions containing 0.5 mM FZ. (The FZ concentration was half that used in actual experiments in order to account for a dilution factor of 2 that occurred on mixing the sample and reagent).

2.4. Fe(II) speciation calculations

Based on the thermodynamic constants given in Table 1, speciation calculations of Fe(II) were performed using Visual Minteq (Gustafsson, 2004). In almost all other studies of the interaction between Fe(II) and phosphate (Cher and Davidson, 1955; Nriagu, 1972; Tamura et al., 1976; Mitra and Matthews, 1985), $\text{FeH}_2\text{PO}_4^+$ and FeHPO_4 have been considered to be the only important Fe(II)-phosphate species, with FePO_4^- either considered to be of negligible importance or not considered at all. However FePO_4^- was considered in the speciation calculations undertaken in this study using a formation constant estimated based on the electrostatic model of ion-pairing by Mattigod and Sposito (1979). This is discussed further and justified in Section 3.

2.5. Estimation of individual oxidation rate constants

The overall oxidation rate constant of Fe(II), k_{app} (in $\text{M}^{-1} \text{ s}^{-1}$), can be described by a rate law of the form:

$$-\frac{d[\text{Fe(II)}]}{dt} = k_{\text{app}}[\text{O}_2][\text{Fe(II)}] \quad (3)$$

$$k_{\text{app}} = 4(k_1\alpha_{\text{Fe}^{2+}} + k_2\alpha_{\text{FeOH}^+} + k_3\alpha_{\text{Fe(OH)}_2} + \dots + k_n\alpha_n) \quad (4)$$

where α_i is the fraction of species i in solution, k_i (in $\text{M}^{-1} \text{ s}^{-1}$) is the second-order rate constant for the oxidation of species i by O_2 , and $[\text{Fe(II)}]$ is the total or analytical Fe(II) concentration. The factor of 4 in Eq. (4) reflects the stoichiometry of Fe(II) oxidation by O_2 when the first oxidation step is rate limiting (King, 1998; Santana-Casiano et al., 2005).

Previous studies (King, 1998; Santana-Casiano et al., 2005; Pham and Waite, 2008b) suggested that Fe^{2+} , FeHCO_3^+ , FeCO_3 , FeCl^+ and FeSO_4 react slowly with O_2 while Fe(OH)^+ , Fe(OH)_2 , $\text{Fe(CO}_3)_2^{2-}$ and $\text{Fe(CO}_3)(\text{OH})^-$ are rapidly oxidized. However, large differences in calculated second-order rate constants for particular Fe(II) species exist between studies, suggesting considerable uncertainty with regard to the actual species contributing to Fe(II) oxidation. In this study, the oxidation of Fe(II) solutions without phosphate was initially investigated and modeled using second-order rate constants for the species FeHCO_3^+ , FeCO_3 , FeCl^+ , FeSO_4 , Fe(OH)^+ , Fe(OH)_2 , $\text{Fe(CO}_3)_2^{2-}$ and $\text{Fe(CO}_3)(\text{OH})^-$ determined previously by Pham and Waite (2008b). The second-order rate constant for the species Fe^{2+} was recalculated for the condition of pH 6.0 and $[\text{PO}_4^{3-}]_T = 0 \text{ mM}$, in which Fe^{2+} and Fe(OH)^+ are the dominant species involved in Fe(II) oxidation. Subsequently, as described above, studies of Fe(II) oxidation in the presence of different phosphate concentrations were undertaken and the second-order rate constants for FePO_4^- , $\text{FeH}_2\text{PO}_4^+$ and FeHPO_4 oxidation estimated

Table 1
Stability constants for Fe(II) speciation model.

Species	log K ($I = 0$, 22 °C)	Reference
$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$	14	1
$\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$	10.3	1
$2\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$	18.1	1
$2\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{H}_2\text{CO}_3$	16.7	1
$\text{H}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{HPO}_4^{2-}$	12.4	2
$2\text{H}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{H}_2\text{PO}_4^-$	19.6	2
$3\text{H}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{H}_3\text{PO}_4$	21.7	2
$\text{Fe}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{FeCO}_3$	5.69	3
$\text{Fe}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{FeHCO}_3^+$	11.8	4
$\text{Fe}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Fe}(\text{CO}_3)_2^{2-}$	7.45	3
$\text{Fe}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{CO}_3)(\text{OH})^- + \text{H}^+$	−4.03	3
$\text{Fe}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})^+ + \text{H}^+$	−9.51	5
$\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{H}^+$	−20.6	5
$\text{Fe}^{2+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^+$	0.3	3
$\text{Fe}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeSO}_4$	2.42	3
$\text{Fe}^{2+} + \text{PO}_4^{3-} \rightleftharpoons \text{FePO}_4$	7.93	6
$\text{Fe}^{2+} + \text{PO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{FeHPO}_4$	16.0	7
$\text{Fe}^{2+} + \text{PO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{FeH}_2\text{PO}_4^+$	22.3	7
$\text{Na}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NaCO}_3^-$	1.27	3
$\text{Na}^+ + \text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NaHCO}_3$	10.1	3
$\text{Na}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{NaSO}_4^-$	1.06	3
$\text{NH}_4^+ + \text{SO}_4^{2-} \rightleftharpoons \text{NH}_4\text{SO}_4^-$	1.03	8

(1) Millero et al. (1995); (2) Stumm and Morgan (1981); (3) King (1998); (4) Millero and Hawke (1992); (5) Morel and Hering (1993); (6) Mattigod and Sposito (1979); (7) Plummer et al. (1976) and (8) Schecher and Mcavoy (1992).

using the least squares method. To evaluate the importance of different species to the overall oxidation of Fe(II), a weighting factor (derived from Eq. (4)) for the contribution of each Fe(II) species, β_i , was introduced:

$$\beta_i = \frac{4k_i\alpha_i}{k_{\text{app}}} \quad (5)$$

where

$$\sum_{i=1}^n \beta_i = \frac{4(k_1\alpha_{\text{Fe}^{2+}} + k_2\alpha_{\text{FeOH}^+} + k_3\alpha_{\text{Fe}(\text{OH})_2} + \dots + k_n\alpha_n)}{k_{\text{app}}} = 1 \quad (6)$$

3. RESULTS AND DISCUSSION

3.1. Overall Fe(II) oxidation rate constants

In all oxidation experiments, the decay of Fe(II) concentration was observed to follow pseudo first-order kinetics. That is,

$$-\frac{d[\text{Fe(II)}]}{dt} = k'[\text{Fe(II)}] \quad (7)$$

where k' (in s^{-1}) is the pseudo first-order rate constant of Fe(II) oxidation ($k' = k_{\text{app}} \times [\text{O}_2]$ according to Eq. (3)).

The solution to this equation is

$$[\text{Fe(II)}]_t = [\text{Fe(II)}]_0 \exp(-k't) \quad (8)$$

Thus k' can be estimated from a plot of $-\ln([\text{Fe(II)}]_t/[\text{Fe(II)}]_0)$ versus t . Linear fits to pH 6.0 data for a range

of $[\text{PO}_4^{3-}]_T$ are shown in Fig. 1, with data at all other pHs and the associated linear fits shown in Fig. EA1.

The pseudo first-order rate constants k' and half times $t_{1/2}$ ($t_{1/2} = \ln(2)/k'$) for the oxidation of 50 nM and 200 nM Fe(II) in solutions of 10 mM buffer, 0.1 M NaCl and 2.0 mM NaHCO_3 over the pH range 6.0–7.8 in the absence and presence of different $[\text{PO}_4^{3-}]_T$ at 22 °C are summarized in Table 2. In agreement with previous investigations, the oxidation of Fe(II) in the absence of phosphate was found to be strongly pH dependent. For example, $t_{1/2}$ for the oxygenation of 200 nM Fe(II) at pH

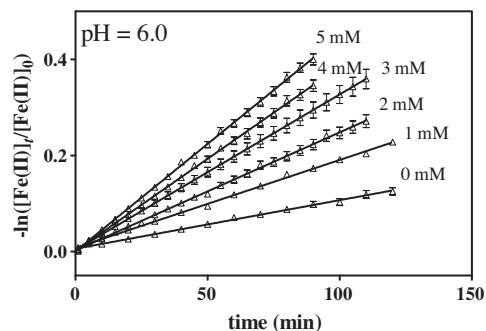


Fig. 1. Linear fitting of $-\ln([\text{Fe(II)}]_t/[\text{Fe(II)}]_0)$ versus time in the presence of various concentrations of phosphate at pH 6.0. $[\text{Fe(II)}]_0 = 200$ nM. $[\text{PO}_4^{3-}]_T$ are shown on the graph panel. Symbols represent the mean value from triplicate experiments. Error bars are the standard error of the mean from triplicate experiments.

Table 2

Pseudo-first order rate constant and half-time for Fe(II) oxidation in the absence and presence of phosphate ions over the pH range 6.0–7.8 at 22 °C.

[Fe(II)] ₀ (nM)	[PO ₄ ³⁻] _T (mM)	log <i>k'</i> (s ⁻¹) ^a					<i>t</i> _{1/2} (min) ^b				
		pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 7.8	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 7.8
200	0	-4.77 ± 0.07	-4.28 ± 0.02	-3.63 ± 0.02	-3.17 ± 0.01	-2.59 ± 0.01	680	219	49.1	17.0	4.5
	1	-4.52 ± 0.01	-3.99 ± 0.02	-3.45 ± 0.02	-2.91 ± 0.03	-2.42 ± 0.08	381	112	32.4	9.4	3.1
	2	-4.40 ± 0.05	-3.87 ± 0.02	-3.31 ± 0.02	-2.74 ± 0.02	-2.30 ± 0.03	289	85.3	23.5	6.3	2.3
	3	-4.28 ± 0.1	-3.78 ± 0.01	-3.25 ± 0.06	-2.62 ± 0.02	-2.22 ± 0.01	219	69.3	20.5	4.8	1.9
	4	-4.20 ± 0.03	-3.66 ± 0.01	-3.09 ± 0.02	-2.52 ± 0.03	-2.16 ± 0.01	182	52.6	14.2	3.8	1.7
	5	-4.13 ± 0.02	-3.60 ± 0.01	-3.04 ± 0.01	-2.46 ± 0.03	-2.11 ± 0.01	155	45.8	12.6	3.3	1.5
50	10	-4.01 ± 0.03	-3.45 ± 0.02	-2.76 ± 0.03	–	–	120	32.7	6.7	–	–

^a Mean ± standard error of the mean from triplicate experiments.

^b *t*_{1/2} = ln(2)/*k'* where *k'* = *k*_{app} × [O₂ (aq)].

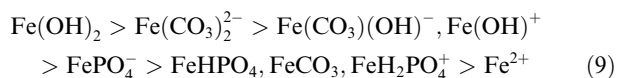
6.0 was about 11 h compared to 4.5 min for the same concentration of Fe(II) at pH 7.8. Except at pH 6.0, the observed oxidation rate constants in the absence of phosphate ions were similar to those obtained previously for the oxygenation of nanomolar concentrations of Fe(II) (Pham and Waite, 2008b). Table 2 also shows that the oxidation of Fe(II) was moderately affected by the concentration of phosphate at all pH values examined. For example, *t*_{1/2} at pH 7.0 decreased from 49.1 min to 12.6 min as [PO₄³⁻]_T increased from 0 mM to 5 mM.

As shown in Fig. 2 (solid lines), log *k*_{app} increased linearly with pH in both the absence and the presence of phosphate. The rapid increase in the oxidation kinetics of Fe(II) with increasing pH in the absence of phosphate has been suggested by King (1998) to be due to changes in Fe(II) speciation, with the concentration of more rapidly oxidized species such as Fe(OH)₂, Fe(CO₃)₂²⁻, and Fe(CO₃)(OH)⁻ increasing at higher pH.

3.2. The speciation model

The distribution of the various Fe(II) species over the range of experimental conditions examined was calculated using the thermodynamic constants presented in Table 1. In general, Fe²⁺, FeCl⁺, FeCO₃, FeHCO₃, FeH₂PO₄⁺, FeHPO₄ and FePO₄⁻ are the dominant Fe(II) species over the pH range 6.0–8.0 while Fe(OH)⁺, Fe(OH)₂, Fe(CO₃)₂²⁻ and Fe(CO₃)(OH)⁻ are minor (Fig. EA2). However the concentrations of Fe(OH)⁺, Fe(OH)₂, Fe(CO₃)₂²⁻, Fe(CO₃)(OH)⁻ and FePO₄⁻ increase drastically with increasing pH compared to the other Fe(II) species. Estimated second-order rate constants for oxygenation of the various Fe(II) species are given in Table 3.

As shown in Fig. 2 (dashed lines), the model output and the experimental data are in excellent agreement over a range of conditions even at high ratios of [PO₄³⁻]_T: [Fe(II)]₀ (Fig. 2G). From these results, we deduce that FePO₄⁻ is considerably more reactive with O₂ (*k* = (2.2 ± 0.2) × 10¹ M⁻¹ s⁻¹) than either FeH₂PO₄⁺ (*k* = (3.2 ± 2) × 10⁻² M⁻¹ s⁻¹) or FeHPO₄ (*k* = (1.2 ± 0.8) × 10⁻¹ M⁻¹ s⁻¹). In addition, the reactivity of Fe(II) species with O₂ estimated in this work follows the following sequence:



According to this sequence, individual rate constants for all the known Fe(II) inorganic complexes considered in this study are larger than the rate constant for free Fe²⁺.

The contribution of individual Fe(II) species to the overall Fe(II) oxidation rate, represented by weighting factor β_{*i*}, is strongly affected by pH and the concentration of phosphate ions (Fig. 3). In the absence of phosphate (Fig. 3A), *k*_{app} is dominated by the contributions of Fe(OH)⁺ and Fe²⁺ at the lowest pH examined (pH 6.0) and Fe(CO₃)₂²⁻, Fe(CO₃)(OH)⁻, and Fe(OH)₂ at the highest pH examined (pH 7.8). However, when phosphate is present (Fig. 3B and C), FePO₄⁻ becomes the major Fe(II) species contributing to the overall rate of Fe(II) oxygenation at all pH values examined. Despite the fact that the existence of FePO₄⁻ has not been independently experimentally verified, its inclusion is critical to successfully modelling Fe(II) oxidation at circumneutral pH when different phosphate concentrations are present; it is not possible to produce reasonable fits to the data over the range of experimental conditions examined when only FeH₂PO₄⁺ and FeHPO₄ are considered in the speciation model.

We attempted to apply the speciation model to describe previous data on the oxidation of micromolar concentrations of Fe(II) (Tamura et al., 1976; Mitra and Matthews, 1985) in the presence of high concentrations of phosphate using the rate constants for individual Fe(II) species estimated in this study (Fig. EA3). Except for the reasonable fit to the data of Tamura et al. (1976) at low pH (4.5) in the presence of 10 μM Fe(II) and either 10 mM or 30 mM phosphate, the model substantially underestimates the previously reported oxidation rates. A possible reason for the difference between the overall rate constants predicted using our model parameters and values determined experimentally previously (Tamura et al., 1976; Mitra and Matthews, 1985) is that solid species such as Fe₃(PO₄)₂(s) and possibly FePO₄(s) may have been present in the previous studies at the high concentrations of Fe(II) and phosphate used, leading to surface catalysis of the oxidation process.

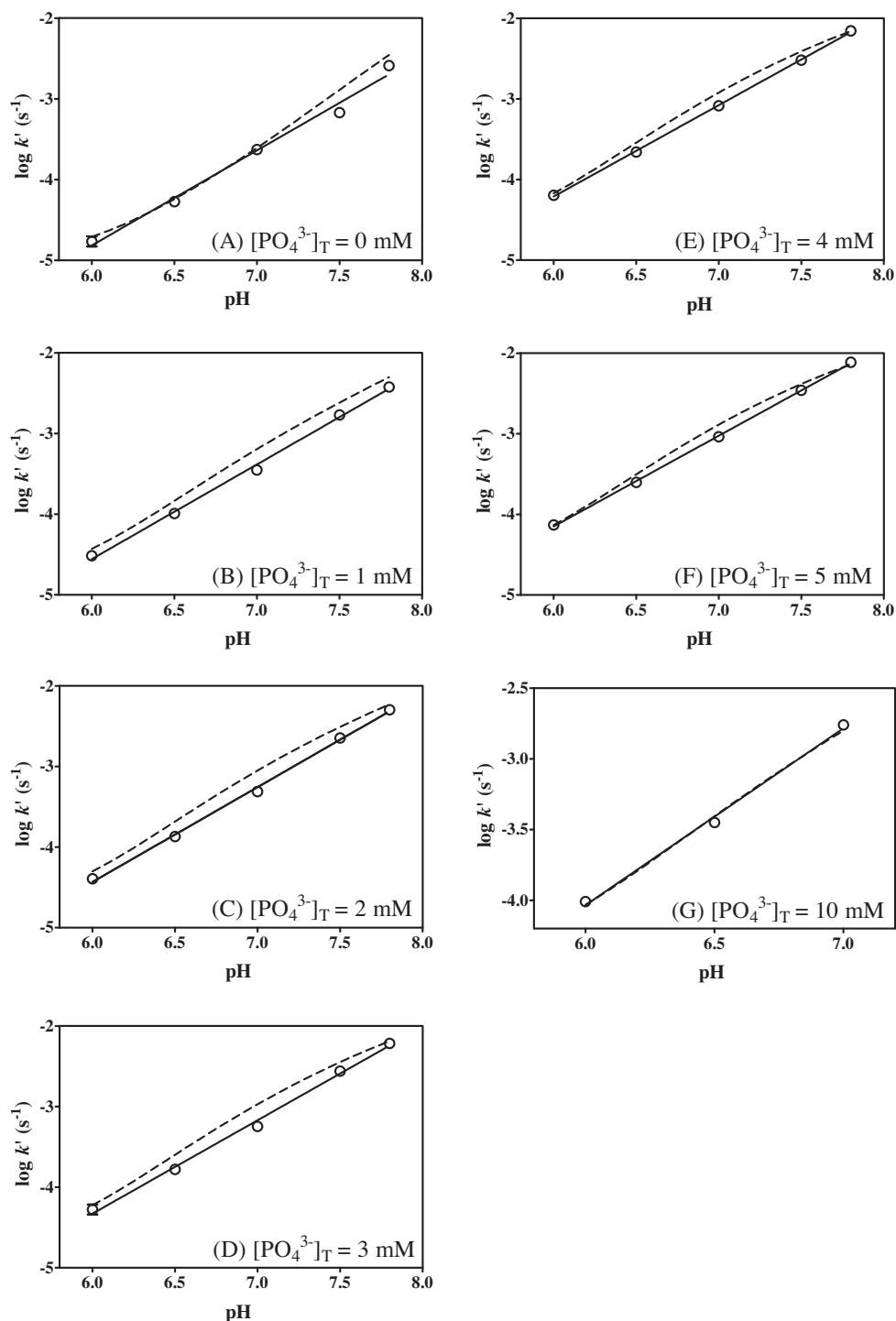


Fig. 2. Linear fitting of $\log k' \text{ (s}^{-1}\text{)}$ vs. pH (solid line) and speciation model predictions of $\log k' \text{ (s}^{-1}\text{)}$ (dashed line) in the absence and presence of phosphate over the pH range 6.0–7.8. $[\text{Fe(II)}]_0 = 200 \text{ nM}$ for A–F and 50 nM for G. Symbols represent the mean value from triplicate experiments. Error bars (which are too small to be visible in this figure) are the standard error of the mean from triplicate experiments.

3.3. Evaluation of rate constants in the context of Marcus Theory

The oxygenation of Fe(II), including Fe(II) complexes, almost certainly proceeds via an outer sphere mechanism,

in which O_2 forms a precursor complex with Fe(II), followed by electron transfer and dissociation of the successor complex, without any change to ligands coordinated in the inner sphere of the molecule (Wehrli, 1990; Rosso and Morgan, 2002). Such outer sphere mechanisms obey a quadratic

Table 3

Individual rate constants for oxidation of Fe(II) species by O₂ at 22 °C and *I* = 0.1.

Fe(II) species	log <i>k_i</i> (M ⁻¹ s ⁻¹) from speciation model approaches ^a				log <i>K</i> _{Fe^{II}L}	log <i>K</i> _{Fe^{III}L} of corresponding Fe(III) species	ΔG_{FeL}^0 (kJ.mol ⁻¹)	log <i>k_i</i> (M ⁻¹ s ⁻¹) from Marcus Theory	
	King (1998) ^b	Santana-Casiano et al. (2005) ^b	Pham and Waite (2008b) ^c	This study ^c				Calculated using $\lambda = 135$ kJ mol ⁻¹	Calculated using $\lambda = 103$ kJ mol ⁻¹
Fe ²⁺	-6.00	-3.00	-0.9	-2.0	—	—	89.7	-5.39	-4.80
Fe(OH) ⁺	0.88	1.00	1.6	1.6	-9.51 ^d	-2.20 ^e	48.0	0.248	1.43
Fe(OH) ₂	5.98	7.18	5.4	5.4	-20.6 ^d	-5.54 ^e	3.80	4.64	6.04
FeHCO ₃ ⁺	<0.16	-2.77	Slow ^f	Slow ^f	11.8 ^g	Unable to be determined			
FeCO ₃	<-0.34	-2.77	0	0	5.69 ^h	9.72 ⁱ	66.7	-2.21	-1.27
Fe(CO ₃) ₂ ²⁻	4.04	4.30	3.6	3.6	7.45 ^h	19.6 ^j	20.4	3.16	4.52
Fe(CO ₃)(OH) ⁻	2.22	2.48	2.3	2.3	-4.03 ^h	7.7 ^j	22.8	2.92	4.27
FeCl ⁺	Slow ^f	-3.00	Slow ^f	Slow ^f	0.3 ^h	1.28 ^e	84.1	-4.43	-3.72
FeSO ₄	Slow ^f	-3.00	Slow ^f	n/a ^k	2.42 ^h	Unable to be determined			
FePO ₄ ⁻	n/a ^k	n/a ^k	n/a ^k	1.3	7.93 ^l	18.9 ^m	27.3	2.45	3.78
FeHPO ₄	n/a ^k	n/a ^k	n/a ^k	-0.91	16.0 ⁿ	22.3 ⁱ	53.7	-0.562	0.549
FeH ₂ PO ₄ ⁺	n/a ^k	n/a ^k	n/a ^k	-1.5	22.3 ⁿ	23.9 ⁱ	80.7	-4.11	-3.36

^a Rate constants were recalculated using the equation $\log k_{\text{app},I} = \log k_{\text{app},0} - 1.338I^{1/2} + 0.5747I$, where $k_{\text{app},I}$ and $k_{\text{app},0}$ are the apparent Fe(II) oxidation rate constants at ionic strength *I* and 0 (King, 1998).

^b Determined at micromolar Fe(II) concentrations.

^c Determined at nanomolar Fe(II) concentrations.

^d Ref. Morel and Hering (1993).

^e Ref. Millero et al. (1995).

^f Too slow to be accurately determined.

^g Ref. Millero and Hawke (1992).

^h Ref. King (1998).

ⁱ Visual Minteq Database (Gustafsson, 2004).

^j Ref. Bruno and Duro (2000).

^k Complex not present in the system studied.

^l Ref. Mattigod and Sposito (1979).

^m The thermodynamic constant for Fe^{III}PO₄ (aq) has not been determined. According to the study of Katsoyiannis and Zouboulis (2002), both phosphate and arsenate present similar affinities for Fe(III); thus in this study, the stability constant of Fe^{III}AsO₄ (Bluteau and Demopoulos, 2007) was adopted for Fe^{III}PO₄(aq).

ⁿ Ref. Plummer et al. (1976).

free energy relationship according to the Marcus Theory, which allows determination of rate constants based on the free energy change of the reactants (Marcus, 1956, 1965; Marcus and Sutin, 1985).

Based on Marcus Theory for an outer-sphere electron-transfer reaction, the relationship between the second-order rate constant, *k* (in M⁻¹ s⁻¹) and the standard free energy of reaction, ΔG^0 , is given by (Ebersson, 1985; Tratnyek and Hoigne, 1994):

$$k = \frac{k_d}{1 + \frac{k_d}{K_d Z} \exp \left[\frac{4}{RT} \left(1 + \frac{\Delta G^0}{\lambda} \right)^2 \right]} \quad (10)$$

where $k_d = 10^{10}$ M⁻¹ s⁻¹ is the diffusion controlled limit, the combined term $\frac{k_d}{K_d Z}$ is typically 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 gas constant $R = 8.314 \times 10^{-3}$ kJ mol⁻¹ K⁻¹, and $T = 298$ K. The reorganization energy λ , which represents the energy required to rearrange the precursor complex into the successor complex during the reaction, has been determined to be 103 kJ mol⁻¹ for inorganic Fe(II) complexes (King and Farlow, 2000) and 135 kJ mol⁻¹ for organic Fe(II) complexes (Rose and Waite, 2003).

The oxidation rate constants of individual Fe(II) species can thus be independently calculated provided ΔG^0 is known. Assuming, reasonably, that the Franck-Condon principle is obeyed (i.e. that electronic transitions occur so rapidly that nuclear coordinates do not change during the transition), the ΔG^0 value for Fe^{II}L oxidation to Fe^{III}L (where L is an inorganic or organic ligand) with concomitant one electron reduction of oxygen to superoxide is given by:

$$\Delta G^0 = -F(E_{\text{O}_2 \rightarrow \text{O}_2^-}^0 - E_{\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}}^0) \quad (11)$$

where $E_{\text{O}_2 \rightarrow \text{O}_2^-}^0 = -0.16$ V (Stanbury, 1989).

The reduction potential $E_{\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}}^0$ may be estimated by applying the Nernst equation (Morel and Hering, 1993) as follows:

$$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}, E_{\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}}^0, \Delta G^0 = -FE_{\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}}^0 \quad (12)$$

$$\text{Fe}^{2+} + \text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}, K_{\text{Fe}^{\text{II}}\text{L}}, \Delta G^0 = -2.303RT \log_{10} K_{\text{Fe}^{\text{II}}\text{L}} \quad (13)$$

$$\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{3+} + \text{L}, 1/K_{\text{Fe}^{\text{III}}\text{L}}, \Delta G^0 = +2.303RT \log_{10} K_{\text{Fe}^{\text{III}}\text{L}} \quad (14)$$

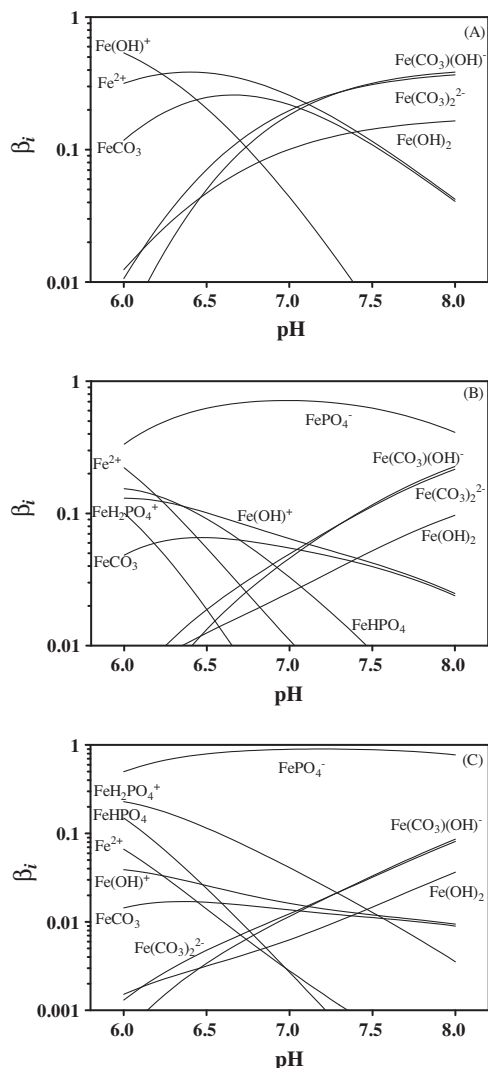
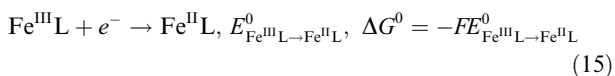


Fig. 3. Weighting factor (β_i) for the relative contribution of Fe(II) species to the overall Fe(II) oxidation rate constant over the pH range 6.0–8.0: A in the absence of phosphate, B with 1 mM $[\text{PO}_4^{3-}]_T$, and C with 5 mM $[\text{PO}_4^{3-}]_T$.



Therefore,

$$-FE_{\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}}^0 = -FE_{\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}}^0 + 2.303RT \log_{10} \left(\frac{K_{\text{Fe}^{\text{III}}\text{L}}}{K_{\text{Fe}^{\text{II}}\text{L}}} \right) \quad (16)$$

or

$$E_{\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe}^{\text{II}}\text{L}}^0 = E_{\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}}^0 - 0.059 \log_{10} \left(\frac{K_{\text{Fe}^{\text{III}}\text{L}}}{K_{\text{Fe}^{\text{II}}\text{L}}} \right) \quad (17)$$

where $E_{\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}}^0 = 0.77\text{V}$ is the standard reduction potential of Fe^{3+} (Schumb et al., 1937) and K_i is the stability constant of the complex i .

Calculated rate constants for all Fe(II) species of interest using different λ values are given in Table 3. Except for

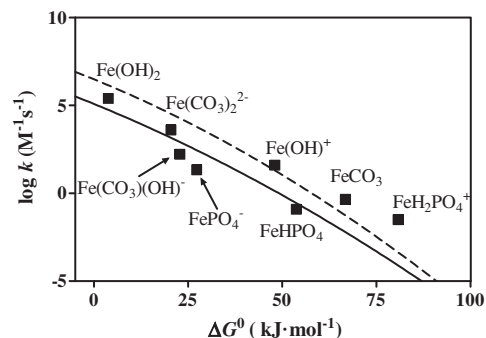


Fig. 4. Comparison of modeled rate constants from this work (symbols) with predictions using Marcus Theory (lines). The dashed line and solid line are predicted from Marcus Theory with $\lambda = 103 \text{ kJ mol}^{-1}$ and 135 kJ mol^{-1} , respectively.

$\text{FeH}_2\text{PO}_4^+$, there is general agreement between the modeled second-order rate constants and predictions from Marcus Theory (Fig. 4). The modeled rate constants for $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{CO}_3)_2^{2-}$, $\text{Fe}(\text{CO}_3)(\text{OH})^-$ and FePO_4^- are comparable to Marcus Theory predictions using $\lambda = 135 \text{ kJ mol}^{-1}$, while the modeled rate constants for FeCO_3 and $\text{Fe}(\text{OH})^+$ are comparable to Marcus Theory predictions using $\lambda = 103 \text{ kJ mol}^{-1}$. This seems reasonable, as it is quite possible that the energy required to reorganize complexes with a greater number of non-aquo ligands, such as $\text{Fe}(\text{CO}_3)(\text{OH})^-$, is higher than that of the simple complexes such as $\text{Fe}(\text{OH})^+$.

The fact that our data follow a relationship consistent with Marcus Theory supports the contention that an outer-sphere electron transfer process controls the oxygenation of Fe(II) species. This, in turn, enables us to predict rates of Fe(II) oxygenation based on the stability of the Fe(II) species present and the stability of the Fe(III) species of similar nuclear configuration.

4. CONCLUSIONS

A model based on a speciation approach has been employed to successfully describe the oxidation of nanomolar concentrations of Fe(II) in the presence of varying concentrations of phosphate ions in NaCl-HCO_3^- buffer solutions at pH 6.0–7.8. The oxidation of Fe(II) was found to depend strongly on pH, but the influence of pH was weaker following the addition of phosphate ions, suggesting that Fe(II)-phosphate species play an important role in the oxidation of Fe(II). The estimated individual kinetic constants for the oxygenation of three Fe(II)-phosphate species were $k = (2.2 \pm 0.2) \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$ for FePO_4^- , $k = (3.2 \pm 2) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for $\text{FeH}_2\text{PO}_4^+$ and $k = (1.2 \pm 0.8) \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for FeHPO_4 . The phosphate complex FePO_4^- was found to be the most important Fe(II) species contributing to the overall rate of Fe(II) oxygenation at high concentrations of phosphate.

We have shown that Fe(II) oxygenation in the presence of phosphate occurs by an outer sphere mechanism with rate constants consistent with those predicted by Marcus Theory. As such, we are able to predict rates of Fe(II) oxygenation based on the thermodynamic stability constants of

the Fe(II) species present and the corresponding Fe(III) species formed on oxidation (which, according to the Franck-Condon principle, will have similar nuclear configuration to the Fe(II) species). Analysis using Marcus Theory suggests the same order of importance with regard to the particular Fe(II)-phosphate species controlling Fe(II) oxidation in the presence of millimolar concentrations of phosphate as is suggested by observed pH dependency of Fe(II) oxidation rate and associated speciation analysis.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2011.05.031](https://doi.org/10.1016/j.gca.2011.05.031).

REFERENCES

- Aitken-Rogers H., Singleton C., Lewin A., Taylor-Gee A., Moore G. and Le Brun N. (2004) Effect of phosphate on bacterioferritin-catalysed iron(II) oxidation. *J. Biol. Inorg. Chem.* **9**, 161–170.
- Amonette J. E. and Templeton J. C. (1998) Improvements to the quantitative assay of nonrefractory minerals for Fe(II) and total Fe using 1,10-phenanthroline. *Clays Clay Miner.* **46**, 51–62.
- Anastacio A. S., Harris B., Yoo H. I., Fabris J. D. and Stucki J. W. (2008) Limitations of the ferrozine method for quantitative assay of mineral systems for ferrous and total iron. *Geochim. Cosmochim. Acta* **72**, 5001–5008.
- Bluteau M. C. and Demopoulos G. P. (2007) The incongruent dissolution of scorodite – solubility, kinetics and mechanism. *Hydrometallurgy* **87**, 163–177.
- Bruno J. and Duro L. (2000) Reply to W. Hummel's comment on and correction to "On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at $T = 25$ degrees C" by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. *Geochim. Cosmochim. Acta* **64**, 2173–2176.
- Cher M. and Davidson N. (1955) The kinetics of the oxygenation of ferrous iron in phosphoric acid solution. *JACS* **77**, 793–798.
- Cutler C., Bravo A., Ray A. D. and Watt R. K. (2005) Iron loading into ferritin can be stimulated or inhibited by the presence of cations and anions: a specific role for phosphate. *J. Inorg. Biochem.* **99**, 2270–2275.
- Ebersson L. (1985) The Marcus theory of electron transfer, a sorting device for toxic compounds. *Adv. Free Radic. Biol. Med.* **1**, 19–90.
- Gibbs C. R. (1976) Characterization and application of ferrozine iron reagent as a ferrous iron indicator. *Anal. Chem.* **48**, 1197–1201.
- Gustafsson J. P. (2004) *Visual MINTEQ*. Windows Version 2.23 ed.
- Harris D. C. and Aisen P. (1973) Facilitation of Fe(II) autooxidation by Fe(III) complexing agents. *Biochim. Biophys. Acta* **329**, 156–158.
- Kandegedara A. and Rorabacher D. B. (1999) Noncomplexing tertiary amines as "better" buffers covering the range of pH 3–11. Temperature dependence of their acid dissociation constants. *Anal. Chem.* **71**, 3140–3144.
- Katsoyiannis I. A. and Zouboulis A. I. (2002) Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. *Water Res.* **36**, 5141–5155.
- King D. W. (1998) Role of carbonate speciation on the oxidation rate of Fe(II) in aquatic systems. *Environ. Sci. Technol.* **32**, 2997–3003.
- King D. W. and Farlow R. (2000) Role of carbonate speciation on the oxidation of Fe(II) by H_2O_2 . *Mar. Chem.* **70**, 201–209.
- Lin J. and Kester D. R. (1992) The Kinetics of Fe(II) complexation by ferrozine in seawater. *Mar. Chem.* **38**, 283–301.
- Marcus R. A. (1956) On the theory of oxidation–reduction reactions involving electron transfer. *J. Chem. Phys.* **24**, 966–978.
- Marcus R. A. (1965) On the theory of electron-transfer reactions. VI: Unified treatment for homogeneous and electrode reactions. *J. Chem. Phys.* **43**, 679–701.
- Marcus R. A. and Sutin N. (1985) Electron transfers in chemistry and biology. *Biochim. Biophys. Acta* **811**, 265–322.
- Mattigod S. V., Sposito G. (1979) Chemical modeling of trace metal equilibria in contaminated soil solutions using the computer program GEOCHEM. In *Chemical Modeling in Aqueous Systems*. American Chemical Society Symposium Series, Vol. 93, pp. 837–856 (Chapter 37).
- Millero F. J. and Hawke D. J. (1992) Ionic interactions of divalent metals in natural waters. *Mar. Chem.* **40**, 19–48.
- Millero F. J., Yao W. S. and Aicher J. (1995) The speciation of Fe(II) and Fe(III) in natural waters. *Mar. Chem.* **50**, 21–39.
- Mitra A. K. and Matthews M. L. (1985) Effects of pH and phosphate on the oxidation of iron in aqueous solution. *Int. J. Pharm.* **23**, 185–193.
- Morel F. M. M. and Hering J. G. (1993) *Principles and Applications of Aquatic Chemistry*. Wiley, New York.
- Nriagu J. O. (1972) Stability of vivianite and ion-pair formation in system $Fe_3(PO_4)_2-H_3PO_4-H_2O$. *Geochim. Cosmochim. Acta* **36**, 459–470.
- Odum W. E. (1988) Comparative ecology of tidal fresh water and salt marshes. *Annu. Rev. Ecol. Syst.* **19**, 147–176.
- Pham A. N. and Waite T. D. (2008a) Oxygenation of Fe(II) in the presence of citrate in aqueous solutions at pH 6.0–8.0 and 25 degrees C: interpretation from an Fe(II)/citrate speciation perspective. *J. Phys. Chem. A* **112**, 643–651.
- Pham A. N. and Waite T. D. (2008b) Oxygenation of Fe(II) in natural waters revisited: kinetic modeling approaches, rate constant estimation and the importance of various reaction pathways. *Geochim. Cosmochim. Acta* **72**, 3616–3630.
- Plummer L. N., Jones B. F., Truesdell A. H., Geological Survey (U.S.), Geological Survey (U.S.). Water Resources Division. (1976) *WATEQF – a FORTRAN IV version of WATEQ: a computer program for calculating chemical equilibrium of natural waters*. Dept. of the Interior, Geological Survey, Water Resources Division, Reston, Va.
- Pullin M. J. and Cabaniss S. E. (2003) The effects of pH, ionic strength, and iron-fulvic acid interactions on the kinetics of nonphotochemical iron transformations. I: Iron(II) oxidation and iron(III) colloid formation. *Geochim. Cosmochim. Acta* **67**, 4067–4077.
- Reinke L. A., Moore D. R., Rau J. M. and Mccay P. B. (1995) Inorganic phosphate promotes redox cycling of iron in liver

- microsomes – effects on free radical reactions. *Arch. Biochem. Biophys.* **316**, 758–764.
- Rose A. L. and Waite T. D. (2002) Kinetic model for Fe(II) oxidation in seawater in the absence and presence of natural organic matter. *Environ. Sci. Technol.* **36**, 433–444.
- Rose A. L. and Waite T. D. (2003) Effect of dissolved natural organic matter on the kinetics of ferrous iron oxygenation in seawater. *Environ. Sci. Technol.* **37**, 4877–4886.
- Rosso K. M. and Morgan J. J. (2002) Outer-sphere electron transfer of metal ion oxidation by molecular oxygen. *Geochim. Cosmochim. Acta* **66**, 4223–4233.
- Santana-Casiano J. M., Gonzalez-Davila M. and Millero F. J. (2005) Oxidation of nanomolar levels of Fe(II) with oxygen in natural waters. *Environ. Sci. Technol.* **39**, 2073–2079.
- Schecher W. D. and Mcavoy D. C. (1992) Mineql+ – a software environment for chemical equilibrium modeling. *Comput. Environ. Urban* **16**, 65–76.
- Schumb W. C., Sherrill M. S. and Sweetser S. B. (1937) The measurement of the molal ferric–ferrous electrode potential. *JACS* **59**, 2360–2365.
- Stanbury D. M. (1989) Reduction potentials involving inorganic free radicals in aqueous solution. In *Advances in Inorganic Chemistry* (ed. A. G. Sykes). Academic Press.
- Stookey L. L. (1970) Ferrozine – a new spectrophotometric reagent for iron. *Anal. Chem.* **42**, 779–781.
- Stucki J. W. (1981) The quantitative assay of minerals for Fe²⁺ and Fe³⁺ using 1,10-phenanthroline. II: A photochemical method. *Soil Sci. Soc. Am. J.* **45**, 638–641.
- Stucki J. W. and Anderson W. L. (1981) The quantitative assay of minerals for Fe²⁺ and Fe³⁺ using 1,10-phenanthroline. I: Sources of variability. *Soil Sci. Soc. Am. J.* **45**, 633–637.
- Stumm W. and Lee G. F. (1961) Oxygenation of ferrous iron. *Ind. Eng. Chem.* **53**, 143–146.
- Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry, an Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd ed. Wiley, J. & Sons Inc., New York.
- Sunda W. G. and Huntsman S. A. (1995) Iron uptake and growth limitation in oceanic and coastal phytoplankton. *Mar. Chem.* **50**, 189–206.
- Svoboda P. and Harms-Ringdahl M. (2002) Kinetics of phosphate-mediated oxidation of ferrous iron and formation of 8-oxo-2'-deoxyguanosine in solutions of free 2'-deoxyguanosine and calf thymus DNA. *Bba-Gen. Subjects* **1571**, 45–54.
- Tamura H., Goto K. and Nagayama M. (1976) Effects of anions on the oxygenation of ferrous ion in neutral solutions. *J. Inorg. Nucl. Chem.* **38**, 113–117.
- Theis T. L. and Singer P. C. (1974) Complexation of iron(II) by organic matter and its effect on iron(II) oxygenation. *Environ. Sci. Technol.* **8**, 569–573.
- Thompsons J. C. and Mottola H. A. (1984) Kinetics of the complexation of iron(II) with ferrozine. *Anal. Chem.* **56**, 755–757.
- Tratnyek P. G. and Hoigne J. (1994) Kinetics of reactions of chlorine dioxide (OCIO) in water. II: Quantitative structure-activity relationships for phenolic compounds. *Water Res.* **28**, 57–66.
- Viollier E., Inglett P. W., Hunter K., Roychoudhury A. N. and Van Cappellen P. (2000) The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Appl. Geochem.* **15**, 785–790.
- Wang X. M. and Waite T. D. (2010) Iron speciation and iron species transformation in activated sludge membrane bioreactors. *Water Res.* **44**, 3511–3521.
- Wehrli B. (1990) Redox reactions of metal ions at mineral surfaces. In *Aquatic Chemical Kinetics* (ed. W. Stumm). Wiley, New York, pp. 311–337.
- Weiss R. F. (1970) Solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.* **17**, 721–735.

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