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The role of Fe(II) species on the oxidation of Fe(II) in natural waters in the presence of O_2 and H_2O_2

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Abstract

The oxidation of Fe(II) at nanomolar levels with O_2, H_2O_2 and their mixtures has been studied and a kinetic model has been applied to describe the experimental results. A first order pH dependence is obtained when the H_2O_2 controls the oxidation, due to the large contributions of $FeOH^+$ and $FeCO_3$ to the overall rate constant. The second order pH dependence for the oxidation of Fe(II) with O_2 is due to the contributions of $Fe(OH)_2$ and $Fe(CO_3)_2^{2-}$ species. Trace amounts of H_2O_2 or O_2 in the solutions radically affect the observed oxidation rates, and the presence of these two oxidants at the same time can explain some deviations obtained from the expected behavior when one of the oxidants is in excess. The experimental data and model results indicate that the oxidation of Fe(II) with H_2O_2 plays a relatively major role in most natural waters. At the pH of seawater, O_2 is the most important oxidant when $[H_2O_2]$ is below 200 nM and [Fe(II)] is at nanomolar levels.

1. Introduction

Over the years a number of authors have studied the rates of oxidation of Fe(II) in different aqueous solutions to understand the behavior of Fe(II) in natural waters at micromolar levels (Stumm and Lee, 1961; Ghost, 1974; Kester et al., 1975; Tamura et al., 1976; Sung and Morgan, 1980; Davison and Seed, 1983; Millero et al., 1987; Moffett and Zika, 1987; Millero and Sotolongo, 1989; Santana-Casiano et al., 2000, 2004) and nanomolar levels (King et al., 1995; Emennegger et al., 1998; King, 1998; King and Farlow, 2000; Rose and Waite, 2002; González-Dávila et al., 2005; Santana-Casiano et al., 2005). The concentration of total dissolved iron (Fe(II) and Fe(III)) that can be present in seawater is influenced by redox conditions of the marine environment. In natural waters both O_2 and H_2O_2 can oxidize Fe(II). The levels of O_2 in surface waters can vary from 71 μM in brines to 210 μM in seawater at 25 °C (Liu and Millero, 2002), while the values of H_2O_2 can vary from 10 to 150 nM in oligotrophic waters to concentrations exceeding 500 nM in coastal waters (Zika et al., 1985a,b; Moore et al., 1993; Hanson et al., 2001). At micromolar levels of Fe(II) the dominant oxidant in natural waters is O_2. However, at nanomolar levels of Fe(II), nanomolar levels of H_2O_2 can be competitive with O_2 (Moffett and Zika, 1987; King and Farlow, 2000).

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The most accepted mechanism used to describe the Fe(II) oxidation with O_2 in natural waters is expressed by Eqs. (1)–(4)

$$\mathrm{Fe(II)} + \mathrm{O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{O_2^{\bullet -}} \tag{1}$$

$$\mathrm{Fe(II)} + \mathrm{O_2^{\bullet -}} \xrightarrow{2H^+} \mathrm{Fe(III)} + \mathrm{H_2O_2} \tag{2}$$

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^{\bullet}} + \mathrm{OH^-} \tag{3}$$

$$\mathrm{Fe(II)} + \mathrm{OH^{\bullet}} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^-} \tag{4}$$

At uM levels of Fe(II), a 4 : 1 stoichiometry with O_2 (Millero et al., 1987; King et al., 1995; King, 1998) and 2 : 1 with H_2O_2 (Moffett and Zika, 1987; Millero and Sotolongo, 1989) has been described, and a pseudo-first-order rate constant k' has been considered

$$\frac{d[\mathrm{Fe(II)}]}{dt} = -k_i'[\mathrm{Fe(II)}] \tag{5}$$

At nanomolar levels of Fe(II), the first-order rate dependence is not always found throughout the total reaction, in particular at the latter stages of the oxidation (King et al., 1995). The value of k' is strongly dependent on pH and the general rate laws valid over most of the pH range of natural waters for O_2 and H_2O_2, respectively, are given by

$$k'_{\mathrm{O_2}} = k_{\mathrm{O_2}}\left[\mathrm{OH^-}\right]^2[\mathrm{O_2}] \tag{6}$$

and

$$k'_{\mathrm{H_2O_2}} = k_{\mathrm{H_2O_2}}[\mathrm{OH^-}][\mathrm{H_2O_2}] \tag{7}$$

At nanomolar Fe(II) concentrations, the rates for all the reactions (1)–(4) need to be considered. The overall rate constants for reactions (1)–(4) are a function of the composition and physical–chemical properties of the solution and are expressed in terms of the weighted sum of the oxidation rates of the individual Fe(II) species

$$\begin{aligned} k = {} & k_{\mathrm{Fe^{2+}}}\alpha_{\mathrm{Fe^{2+}}} + k_{\mathrm{FeOH^-}}\alpha_{\mathrm{FeOH^-}} + k_{\mathrm{Fe(OH)_2}}\alpha_{\mathrm{Fe(OH)_2}} \\ & + k_{\mathrm{FeHCO_3^-}}\alpha_{\mathrm{FeHCO_3^-}} + k_{\mathrm{Fe(CO_3)}}\alpha_{\mathrm{Fe(CO_3)}} \\ & + k_{\mathrm{Fe(CO_3)_2^{2-}}}\alpha_{\mathrm{Fe(CO_3)_2^{2-}}} \\ & + k_{\mathrm{Fe(CO_3)(OH)^-}}\alpha_{\mathrm{Fe(CO_3)(OH)^-}} + k_{\mathrm{FeCl^+}}\alpha_{\mathrm{FeCl^+}} \\ & + k_{\mathrm{FeSO_4}}\alpha_{\mathrm{FeSO_4}} \end{aligned} \tag{8}$$

where α_i is the molar fraction of Fe(II) species in the solution.

Moreover, at nanomolar levels of Fe(II), it is necessary to consider, the back-reaction of Fe(III) with $O_2^{\bullet -}$ (Eq. (9)) (King et al., 1995; Rose and Waite, 2002), the hydrolysis of Fe(III) to form insoluble $Fe(OH)_3$ (Eq. (10)) (Rose and Waite, 2002, 2003) and the scavenging of $O_2^{\bullet -}$ by nanomolar concentrations of inorganic Cu(II) present in the solution (Eqs. (11) and (12)) (Rose and Waite, 2002). Rose and Waite (2002) studied the Fe(II) oxidation in seawater at nanomolar concentrations at a fixed pH (8.09) and salinity (42.7) considering the above mentioned processes. The superoxide ($O_2^{\bullet -}$) and $OH^{\bullet}$ intermediates produced in the Fe(II) oxidation can also be effective as oxidants for other reduced compounds (Br^-, Cl^-, HCO_3^- and dissolved organic matter) (McElroy, 1990; Emmenegger et al., 1998). The newly generated radicals can perform the role of $OH^{\bullet}$ intermediates in reaction (4), as the radical derivatives are likely to also be extremely reactive (King et al., 1995; Emmenegger et al., 1998).

$$\mathrm{Fe(III)} + \mathrm{O_2^{\bullet -}} \rightarrow \mathrm{Fe(II)} + \mathrm{O_2} \tag{9}$$

$$\mathrm{Fe(III)} + 3\mathrm{OH^-} \rightarrow \mathrm{Fe(OH)_3(s)} \tag{10}$$

$$\mathrm{Cu(II)} + \mathrm{O_2^{\bullet -}} \rightarrow \mathrm{Cu(I)} + \mathrm{O_2} \tag{11}$$

$$\mathrm{Cu(I)} + \mathrm{O_2^{\bullet -}} + 2\mathrm{H^+} \rightarrow \mathrm{Cu(II)} + \mathrm{H_2O_2}. \tag{12}$$

In previous work (González-Dávila et al., 2005; Santana-Casiano et al., 2005), the authors have studied in detail the oxidation of Fe(II) with H_2O_2 and O_2 in seawater at nanomolar levels as a function of pH, HCO_3^- concentration, temperature and salinity. Measurements also have been made in pure water and NaCl solutions with different bicarbonate concentrations. A kinetic model has been applied which includes all the reactions mentioned above. The model allows one to describe the rates of individual reactions in terms of the species of Fe(II) in the solutions (Fe^{2+}, $Fe(OH)^+$, $Fe(OH)_2$, $FeCO_3$ and $Fe(CO_3)_2^{2-}$). This work focuses on the study of the role played by the different Fe(II) species on the oxidation of Fe(II) at nanomolar levels in the presence of H_2O_2, O_2 and trace amounts of both oxidants.

2. Experimental

2.1. Chemicals

The seawater used in this study was collected in the Gulf Stream off the coast of Florida. The practical salinity was determined by using an Autosal™ salinometer. Dilutions were made with Milli-Q ion exchanged water (18 MΩ). Fe(II) stock solutions (2×10^{-3} and 4×10^{-4} M) were prepared using ferrous ammonium sulfate hexahydrate (Fisher), acidified with Suprapur HCl to pH = 2. In most of the studies, the initial concentrations of Fe(II) were kept at 250 nM in the reaction vessel. Some studies were made with an initial Fe(II) concentration of 20, 30 and 50 nM. All the chemicals used for the Fe(II) determination were trace analytical grade.

2.2. Oxidation experiments

The reactions were studied in a 250 ml glass thermostated vessel as shown elsewhere (González-Dávila et al., 2005; Santana-Casiano et al., 2005). When it was necessary to remove the dissolved oxygen, the solution was bubbled with N_2 for one and a half hours. In all cases, the gas stream passed through a MnO_4^- solution to eliminate any H_2O_2 and through a trap with MilliQ-18 MΩ pure water. The pH of the solution was determined on the free scale, pH_F, following Millero (1986). The pH was adjusted to the desired value with additions of small amounts of 1 M HCl and the required amount of H_2O_2 was added to the seawater. The addition of the Fe(II) stock solution (25 μl) to the seawater corresponds to the zero time of the reaction. The pH for the study was recorded during the reaction to account for any change after the addition of the Fe(II). The changes in pH were always less than 0.02, with the highest effects occurring at low pH where the buffer capacity of the carbonate is lowest.

2.3. Fe(II) analysis

The Fe(II) concentrations were determined spectrophotometrically using a modified version of the ferrozine method (Viollier et al., 2000) as discussed elsewhere (González-Dávila et al., 2005; Santana-Casiano et al., 2005). Briefly, samples react with ferrozine in an acetate buffer (pH = 5.5) to form a pink Fe(II)–ferrozine complex that absorbs at 562 nm.

A 5 m long waveguide capillary flow cell (LWCFC) from World precision instruments connected to the UV detector S2000 (Ocean Optics™) was used to make the measurements of Fe(II) at nanomolar levels (Zhang et al., 2001). The standard error for the Fe(II) determination is σ 1.0 nM of [Fe(II)].

2.4. O_2 and H_2O_2 determination

Dissolved oxygen concentrations in seawater were determined in each experiment using a modified Winkler method described by Hansen (Hansen, 1999). Hydrogen peroxide was determined using an enzyme-mediated fluorescent decay method utilizing horseradish peroxidase and scopoletin with a Turner Designs model 10 fluorometer (Zika and Saltzmann, 1982; Moore et al., 1993).

2.5. Numerical model

The kinetic model uses the Gepasi Version 3.21 software (Mendes, 1997) to simulate the chemical kinetics, and to compute the time-dependent concentra-

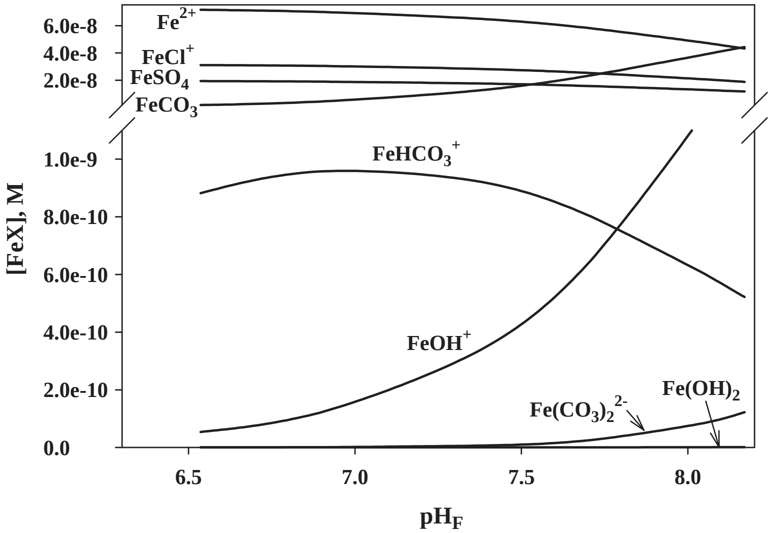

Fig. 1. Fe(II) speciation in seawater media with an ionic strength of 0.7 M.

tions of all the reactants as is described in González-Dávila et al. (2005) and Santana-Casiano et al. (2004, 2005). The Statistica Program for Windows (1995) was used in the minimization procedure.

3. Results and discussion

The speciation of Fe(II) in seawater is shown in Fig. 1. The dissociation and complex formation equilibrium constants for the reaction of Fe(II) species with the different major inorganic species in seawater are given in Table 1 (González-Dávila et al., 2005). In the pH range studied (6.5 to 8.2), for a total Fe(II) concentration of 1.25×10^{-7} M, the Fe(II) speciation is dominated by the Fe^{2+}, $FeCl^+$ and $FeSO_4$ species. At a pH higher than 8.2, the $FeCO_3$ species becomes important. In addition, the concentrations of $FeOH^+$ and $Fe(OH)_2$ increase with the pH reaching values of 1.1 nM $FeOH^+$ and 0.79 pM $Fe(OH)_2$ at pH 8. The concentrations of $Fe(CO_3)OH^-$ and $Fe(CO_3)_2^{2-}$ also increase with increasing pH, reaching levels of 3.3 and 0.08 nM, respectively, at pH 8.

The individual species play a different roles in the overall oxidation rate of Fe(II) depending on the value of their individual rates of oxidation. To understand this behavior, we will first consider the oxidation of Fe(II) with H_2O_2, second with O_2 and third with both O_2 and H_2O_2.

3.1. Oxidation of Fe(II) with H_2O_2

The oxidation of Fe(II) with H_2O_2 takes place through the Eqs. (3) (4) by the previously mentioned mechanism (Moffett and Zika, 1987; Millero and Sotolongo, 1989). The oxidation of Fe(II) is a strong function of pH from 6.5 to 8.2 as shown in Fig. 2 and listed

Table 1
Stability constants for the formation of Fe(II) and Fe(III) inorganic complexes considered for the kinetic model

N°	Species	Log K (0.7 mol L^{-1}, 25 °C)	Ref
1	$H_2O \Leftrightarrow H^+ + OH^-$	−13.69	1
2	$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$	−6.005	1
3	$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$	−9.6	1
4	$Na^+ + HCO_3^- \Leftrightarrow NaHCO_3$	−0.53	2
5	$Na^+ + CO_3^{2-} \Leftrightarrow NaCO_3^-$	−0.42	2
6	$Ca^{2+} + HCO_3^- \Leftrightarrow CaHCO_3^+$	0.33	2
7	$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3$	2.1	2
8	$Mg^{2+} + HCO_3^- \Leftrightarrow MgHCO_3^+$	0.28	2
9	$Mg^{2+} + CO_3^{2-} \Leftrightarrow MgCO_3$	1.94	2
10	$2\ Mg^{2+} + CO_3^{2-} \Leftrightarrow Mg_2(CO_3)^{2+}$	2.59	2
11	$Mg^{2+} + OH^- \Leftrightarrow MgOH^+$	1.70	2
12	$Fe^{2+} + HCO_3^- \Leftrightarrow FeHCO_3^+$	0.97	3
13	$Fe^{2+} + CO_3^{2-} \Leftrightarrow FeCO_3$	4.33	4
14	$Fe^{2+} + 2CO_3^{2-} \Leftrightarrow Fe(CO_3)_2$	6.09	4
15	$Fe^{2+} + CO_3^{2-} + OH^- \Leftrightarrow Fe(CO_3)(OH)^-$	8.90	4
16	$Fe^{2+} + H_2O \Leftrightarrow Fe(OH)^+ + H^+$	−9.66	5
17	$Fe^{2+} + 2 \cdot H_2O \Leftrightarrow Fe(OH)_2 + 2H^+$	−20.87	5
18	$Fe^{2+} + Cl^- \Leftrightarrow FeCl^+$	−0.12	4
19	$Fe^{2+} + SO_4^{2-} \Leftrightarrow FeSO_4$	0.96	4
20	$H^+ + SO_4^{2-} \Leftrightarrow HSO_4^-$	−0.10	1
21	$Fe^{3+} + Cl^- \Leftrightarrow FeCl^{2+}$	0.57	5
22	$Fe^{3+} + 2\ Cl^- \Leftrightarrow FeCl_2^+$	0.13	5
23	$Fe^{3+} + H_2O \Leftrightarrow Fe(OH)^{2+} + H^+$	−2.62	5
24	$Fe^{3+} + 2 \cdot H_2O \Leftrightarrow Fe(OH)_2^+ + 2H^+$	−6.0	5
25	$Fe^{3+} + 3 \cdot H_2O \Leftrightarrow Fe(OH)_3 + 3H^+$	−12.5	5
26	$Fe^{3+} + 4 \cdot H_2O \Leftrightarrow Fe(OH)_4^- + 4H^+$	−21.8	5
27	$Fe(II) + O_2^{\bullet -} + 2H^+ \rightarrow Fe(III) + H_2O_2$	7.00	6
28	$Fe(III) + O_2^{\bullet -} \rightarrow Fe(II) + O_2$	8.18	6
29	$Fe(III) + 3OH^- \rightarrow Fe(OH)_3(s)$	4.40	7
30	$Cu(II) + O_2^{\bullet -} \rightarrow Cu(I) + O_2$	8.82	8
31	$Cu(I) + O_2^{\bullet -} + 2H^+ \rightarrow Cu(II) + H_2O_2$	9.30	8

1. Millero, 1995. 2. Millero and Schreiber, 1982. 3. Millero and Hawke, 1992. 4. King, 1998. 5. Millero et al., 1995. 6. Rush and Bielski, 1985. 7. Rose and Waite, 2002. 8. Zafiriou et al., 1998.

Rate constants for reactions (9)–(12) in the text (nos. 28–31) are also included. The value for the reaction no. 27 was used at pH = 8.0 as a condition to be followed by the model for the total inorganic Fe(II).

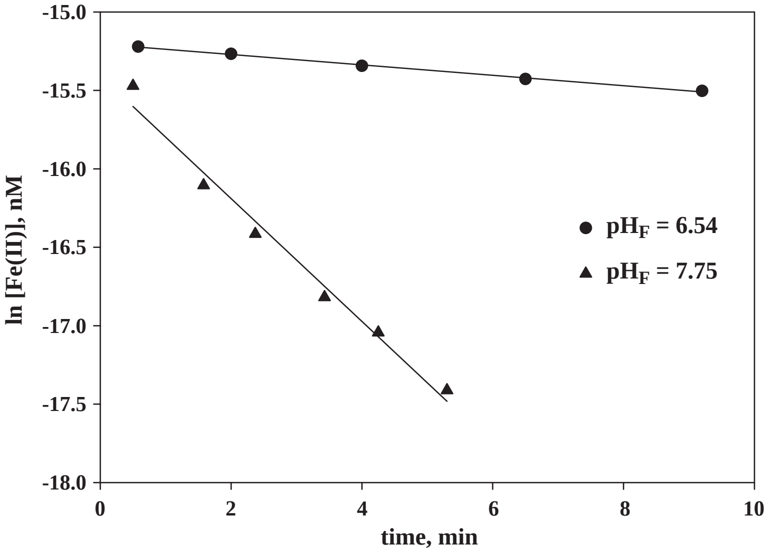

Fig. 2. Fe(II) concentration evolution as a function of time at pH 7.75 and 6.54 with initial [Fe(II)] = 250 nM and $[H_2O_2]$ = 275 nM.

in Table 2. For a Fe(II) : H_2O_2 ratio above 2 : 1 at 25 °C (250 and 275 nM), a pseudo-first order rate is found (Eq. (5)) (Moffett and Zika, 1987; Millero and Sotolongo, 1989). At values of pH below 7.5, a pseudo-first order rate for the Fe(II) oxidation is observed at times longer than $t_{1/2}$. At a pH above 7.5 a deviation from the pseudo-first order is observed at times longer than $t_{1/2}$. An increased role of the traces amount of oxygen and changes in the Fe(II) speciation could account for a higher order of the reaction at pH > 7.5. The values of log k ($k = k_1\ [H_2O_2]^{-1}$) assuming a pseudo-first order rate at times lower than $t_{1/2}$ over the entire pH range, have been fitted to the linear equation

$$\log k = -2.55(\pm 0.09) + 0.89(\pm 0.01)\mathrm{pH}$$

The individual rate constants for the oxidation of Fe(II) with H_2O_2 were obtained by applying a kinetic model to all the experimental results at different pH

Table 2

Pseudo-first order rate constants for the oxidation of Fe(II) by O_2 and H_2O_2 at 25 °C in seawater (DOC = 87 μM, S = 36.2, $[HCO_3^-]$ = 2.05 mM)

Media			pH	log k (s^{-1})
$[Fe(II)]_o$ = 250 nM $[O_2]$ = 17 μM $[H_2O_2]$ = 275 nM			8.17	−1.75
			7.94	−2.02
			7.71	−2.19
			7.36	−2.50
			6.99	−2.85
			6.70	−3.11
			6.54	−3.26
		$[H_2O_2]$ = 72.5 nM	8.17	−2.52
		$[H_2O_2]$ = 106 nM	8.17	−2.34
		$[H_2O_2]$ = 474 nM	8.17	−1.50
$[Fe(II)]_o$ = 250 nM $[O_2]$ = 210 μM $[H_2O_2]$ = 30 nM			8.17	−2.09
			7.99	−2.42
			7.69	−3.03
			7.47	−3.33
			6.49	−4.01
		$[H_2O_2]$ = 50 nM	8.17	−1.90
		$[H_2O_2]$ = 150 nM	8.17	−1.59
		$[H_2O_2]$ = 250 nM	8.17	−1.49
$[Fe(II)]_o$ = 50 nM	$[O_2]$ = 210 μM	$[H_2O_2]$ = 20 nM	8.00	−2.44
$[Fe(II)]_o$ = 30 nM	$[O_2]$ = 210 μM	$[H_2O_2]$ = 20 nM	8.00	−2.44
$[Fe(II)]_o$ = 30 nM	$[O_2]$ = 210 μM	$[H_2O_2]$ = 55 nM	8.00	−2.29
$[Fe(II)]_o$ = 30 nM	$[O_2]$ = 210 μM	$[H_2O_2]$ = 90 nM	8.00	−2.11

Table 3
Fe(II) oxidation rate constants (log k) with oxygen and superoxide in seawater (M^{-1} min^{-1}) valid for the pH range 6 to 8.2 and 25 °C calculated from the kinetic model

Species	O_2	$O_2^{\bullet -}$	H_2O_2
Fe^{2+}	0.544	3.84	2.38
$FeHCO_3^+$	−1.0	0.31	<1.2
$FeCO_3$	0.60	2.94	4.27
$Fe(CO_3)_2^{2-}$	3.69	9.60	7.19
$Fe(CO_3)OH^-$	1.87	2.54	<1.7
$FeOH^+$	2.38	4.96	6.20
$Fe(OH)_2$	6.06	12.18	9.30

Oxidation rates with hydrogen peroxide ($k_{app,H_2O_2} = 2\ k_{H_2O_2}$) are from González-Dávila et al. (2005). The $FeCl^+$ and $FeSO_4$ species are inactive in all cases.

(6.5 to 8.2) and HCO_3^- concentrations (seawater value = 2.05, 2.95 and 4.05 mM) (González-Dávila et al., 2005). The addition of HCO_3^- affects the Fe(II) speciation and causes the rates of oxidation of Fe(II) with H_2O_2 to increase (Millero et al., 1991; King and Farlow, 2000). Values for the individual rate constants that fit the experimental data are those determined by González-Dávila et al. (2005) and are given in Table 3. The non-pH dependence species $FeCl^+$ and $FeSO_4$ were considered to be non-reactive. The rate of the reaction between Fe(II) and the hydroxyl radical ($OH^\bullet$) or any other free radical is likely to be extremely fast (King et al., 1995; Emmenegger et al., 1998; Rose and Waite, 2002) and the stoichiometric with respect to Fe(II) was assumed to be $k_{app,H_2O_2} = 2\ k_{H_2O_2}$.

The agreement between experimental data and model results under different experimental conditions (González-Dávila et al., 2005) at different levels of HCO_3^- and pH are shown in Fig. 3. The lines represent the output from the kinetic model, and validate the rate constants presented in Table 3. Fig. 4 shows the contributions of the different Fe(II) species to the total overall Fe(II) oxidation. For the pH range of this study, $FeOH^+$ is the most important contributing species to the overall oxidation rate while $FeCO_3$ contributes half of the $FeOH^+$ value. These two Fe(II) species are consistent with the first order pH-dependence on Fe(II) of the rates found in previous studies (Moffett and Zika, 1987; Millero and Sotolongo, 1989). At pH values higher than 8, the $Fe(OH)_2$ and $Fe(CO_3)_2^{2-}$ species contribute over 20% to the rates. The $Fe(OH)_2$ complex is the most important species at pH higher than 8.1. Thus, in seawater at low pH the first order pH dependence is due to the $FeOH^+$ complex; while at high pH the higher contribution of $Fe(OH)_2$ and $Fe(CO_3)_2^{2-}$ complexes cause the rates to be second order. This is similar to the oxidation of Fe(II) with O_2 in seawater (Millero et al., 1987). This effect is most important at low concentrations of H_2O_2.

In an attempt to avoid the presence of O_2, all the experiments were carried out in solutions bubbled with N_2 for one and a half hours. Initially the presence of O_2 was neglected and the Eqs. (1) (2) were not considered in the model. However some deviations were observed between the experimental and modeled data, in partic-

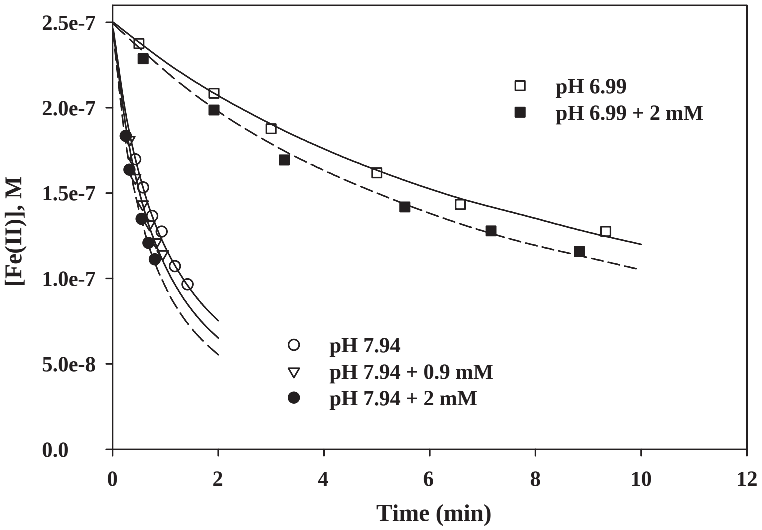

Fig. 3. Experimental and predicted Fe(II) concentration at pH_F 6.99 and 7.94 in the presence of different $NaHCO_3$ concentrations at 25 °C using the kinetic model and constants presented in Table 2.

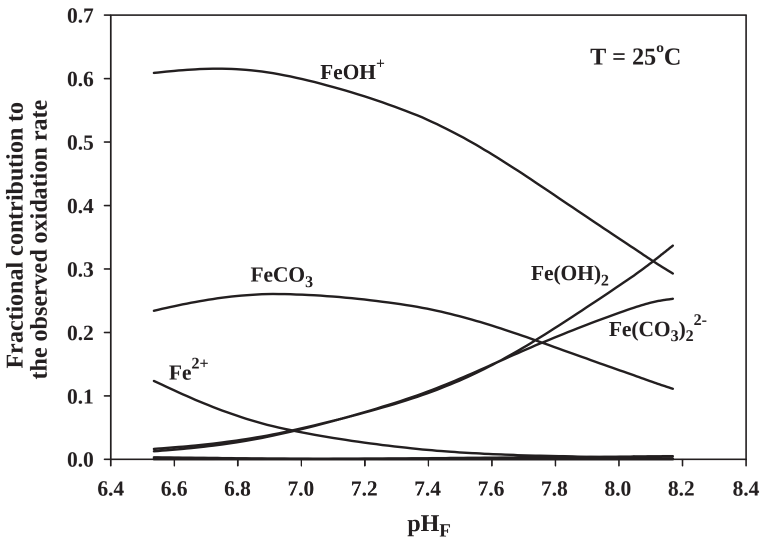

Fig. 4. Contribution of specific Fe(II) species in total Fe(II) oxidation rate by hydrogen peroxide in seawater (S=36.2) and 25 °C.

ular at low [H_2O_2]. Only when the trace amount of O_2 that remained in the solution (17 µM, Table 2) was considered and the oxidation of the different Fe(II) species with molecular oxygen were also included in the kinetic model, did the model fit the experimental data. This amount of O_2 has been neglected in all the studies using high amounts of H_2O_2. By considering the amount of O_2 in the solutions, faster oxidation rates were obtained and give a good fit of the experimental results (the dashed lines in Fig. 5). From the model, we can conclude that when the dissolved O_2 : H_2O_2 ratio is higher than 100, the oxidation with oxygen becomes important and needs to be considered. In most of our studies, the O_2 : H_2O_2 ratio was 60 and the values predicted by the model with and without considering the O_2 contribution are within the estimated error.

3.2. Oxidation of Fe(II) with O_2

The Fe(II) species that are important for the oxidation with O_2 are different than found with H_2O_2 (Fig. 6). The kinetic model was applied by considering all reactions

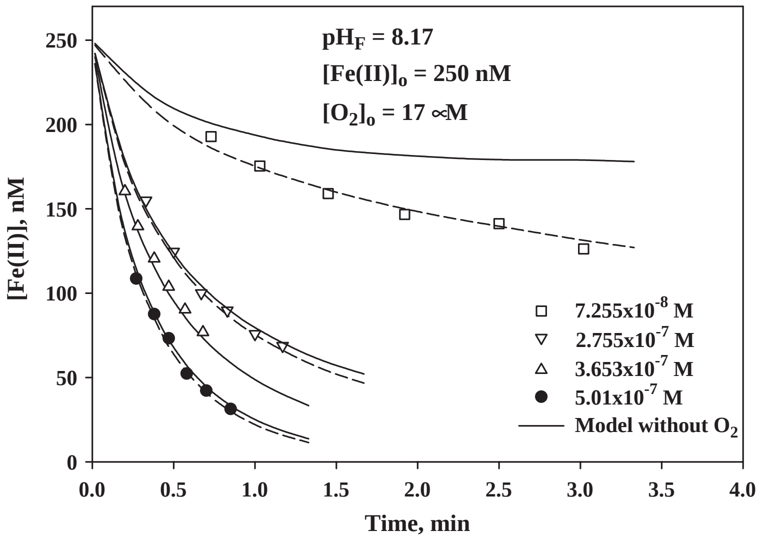

Fig. 5. Effect of [H_2O_2] concentration in the oxidation of Fe(II) in seawater (S=36.2, pH$_F$=8.17, T=25 °C). Lines represent model output considering both the absence of dissolved O_2 (solid lines) and the presence of O_2 after bubbling with nitrogen at the concentration of 17 µM (dashed lines).

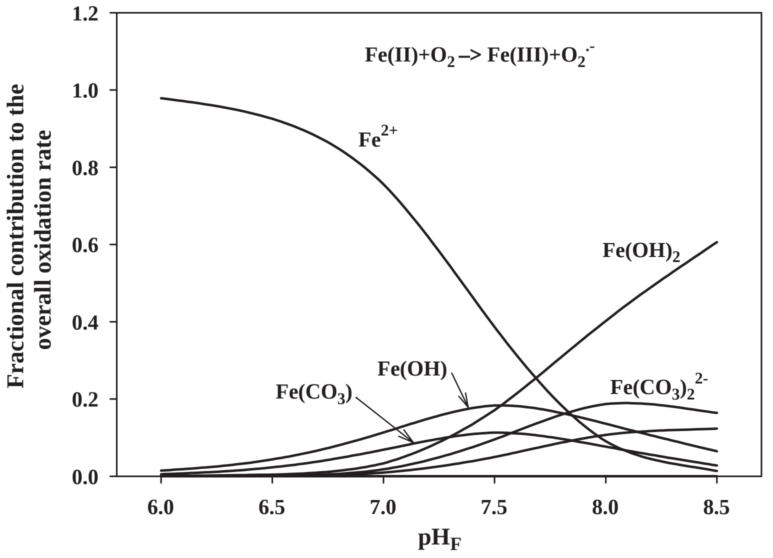

Fig. 6. Contribution of specific Fe(II) species in total Fe(II) oxidation rate by oxygen in seawater (S = 36.1) and 25 °C.

previously described (Eqs. (1)–(4), (9)–(12)) for each individual Fe(II) species. The values considered for reactions (9)–(12) are those given in Table 1. The set of constants that best fit the experimental results are given in Table 3 for the oxidation of Fe(II) with both O_2 and superoxide radical ($O_2^{\bullet-}$), together with the rate constants for the oxidation with H_2O_2. An initial H_2O_2 concentration of 30 nM and 0.4 nM of inorganic complexed Cu (González-Dávila and Millero, 1990) were considered when the model was applied to seawater.

The contributions of the different Fe(II) species to the oxidation rate with O_2 are shown in Fig. 6. At a pH over 7.7, $Fe(OH)_2$ is the most important species, reaching 50% at pH = 8.2, while $Fe(CO_3)_2^{2-}$ contributes 20%. At a pH lower than 7.7, Fe^{2+} is the most important species with more than 80% at a pH below 7. Fig. 7 shows the contributions of the different Fe(II) species to the oxidation rate with $O_2^{\bullet-}$. The overall rates are dominated (over 80%) by the $Fe(OH)_2$ species at a pH over 6.5. $Fe(CO_3)_2^{2-}$ reaches a value of 20% around pH = 7.5. Both species show a second-order pH depen-

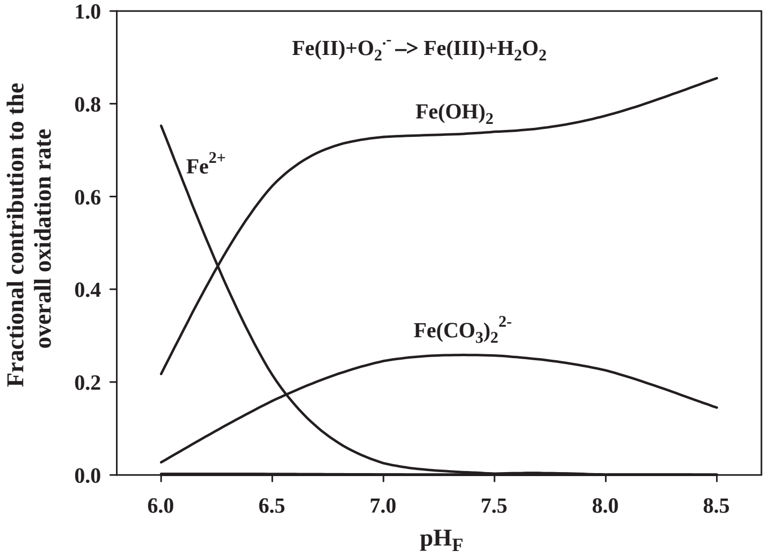

Fig. 7. Contribution of specific Fe(II) species in total Fe(II) oxidation rate by superoxide in seawater (S = 36.1) and 25 °C.

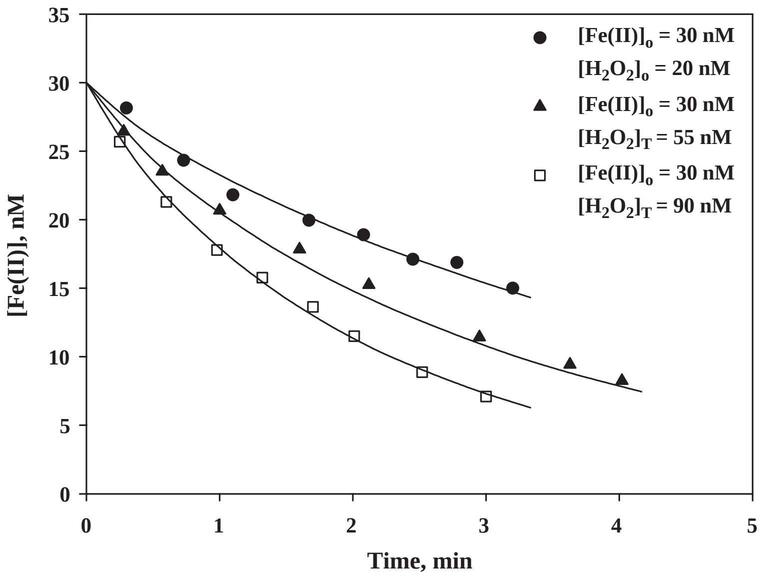

Fig. 8. Experimental and predicted Fe(II) concentrations at 30 nM Fe(II) initial concentration with different concentrations of H_2O_2 in natural seawater ($[NaHCO_3]_T$=2.05 mM), using the kinetic model and constants presented in Table 2.

dence which is consistent with the second-order dependence with the pH for the oxidation rate (Millero et al., 1987).

As was the case with H_2O_2, the oxidation of Fe(II) with O_2 one needs to consider trace amounts of H_2O_2 present in the solution (Table 2). The oxidation rates are increased even with very low concentrations of hydrogen peroxide. The agreement between experimental measurements and model predictions is shown in Fig. 8.

3.3. Oxidation of Fe(II) with O_2 and H_2O_2

According to previous work (Moffett and Zika, 1987; Emmenegger et al., 1998; King and Farlow, 2000) and the results presented here, both O_2 and

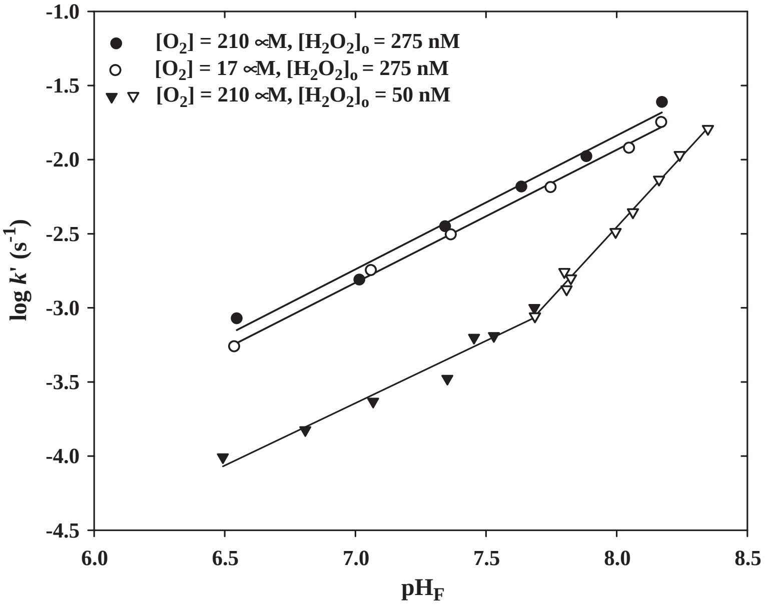

Fig. 9. Effect of pH on the pseudo-first order oxidation rate constants (log k', s^{-1}) in oxygen saturated ($[O_2]$=210 μM) and N_2-bubbled ($[O_2]$=17 μM) seawater, at 275 and 50 nM $[H_2O_2]_o$ concentration.

H_2O_2 can compete for the oxidation of Fe(II). This can be represented by

$$k'^{*} = k_{O_2}[O_2]\Big[OH^-]^2 + k_{H_2O_2}[H_2O_2][OH^-]$$

The second term in Eq. (14) can become more effective than the first term at values of pH below 7.5. Under these conditions,

$$k'^{*}k_{H_2O_2}[H_2O_2][OH^-].$$

The log of the pseudo-first-order rate constants in the pH range where Eq. (15) is valid should give a first order dependence of pH. The results presented in Fig. 9 and listed in Table 2 yield a slope of 0.90 ± 0.05 when $[H_2O_2]$ is over the stoichiometric 2 : 1 ratio (275 nM), and is independent of the O_2 concentration (210 or 17 μM). At H_2O_2 concentrations, about 50 nM, in oxygen saturated seawater, the slope as a function of the pH below 7.7, does not change. Only when the pH is over 7.7, conditions typically found in oceanic seawater, one finds a second-degree pH dependence with a slope 1.92 ± 0.06, showing that oxygen dominates the oxidation rate.

In order to described the Fe(II) species controlling the oxidation process with both O_2 and H_2O_2 at nanomolar Fe(II) and explain the pH dependence shown

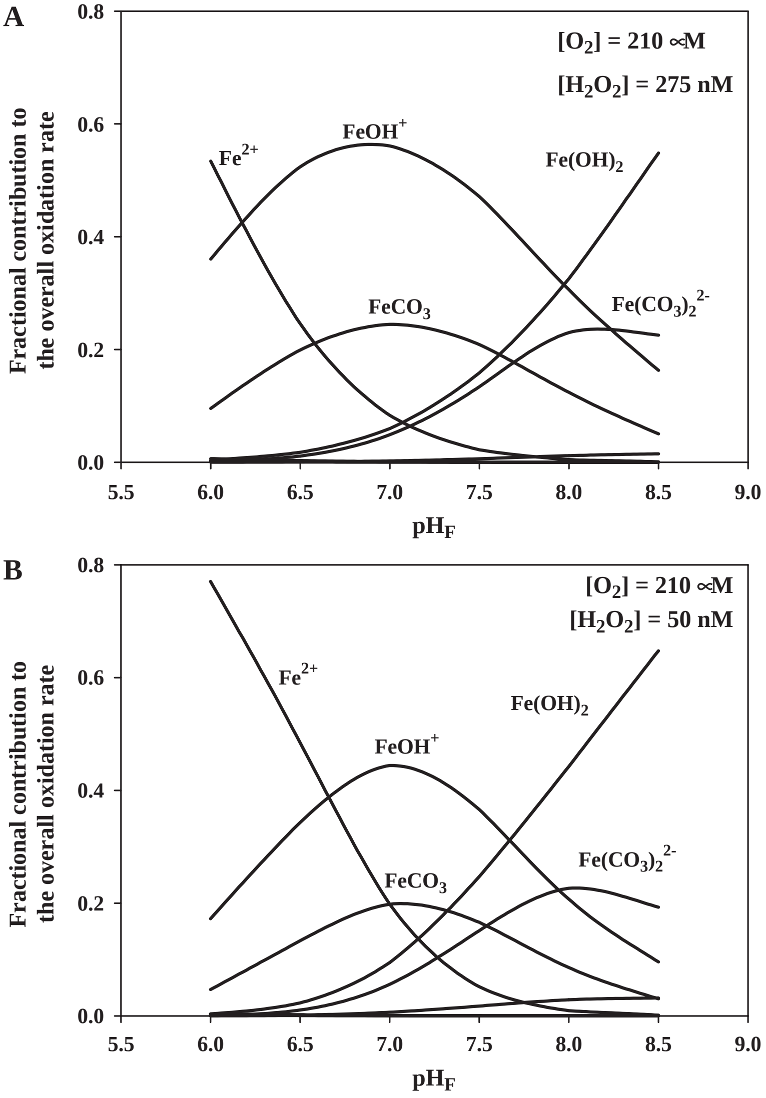

Fig. 10. Contribution of specific Fe(II) species in the total Fe(II) oxidation rate in seawater with $[O_2]$=210 μM, $[Fe(II)]_o$=250 nM and A) $[H_2O_2]_o$=275 nM and B) $[H_2O_2]_o$=50 nM.

above, it is also important to know how each species participates in the process.

$$-\frac{d\{\mathrm{Fe(II)}\}}{dt} = \sum_j k_{\mathrm{app},j}[\mathrm{Oxidant}]_j[\mathrm{Fe(II)}]$$

$$= \left(k_{\mathrm{app,O_2}}[\mathrm{O_2}] + k_{\mathrm{app,H_2O_2}}[\mathrm{H_2O_2}]\right)[\mathrm{Fe(II)}] \qquad (16)$$

$$k_{\mathrm{app},j} = \sum_i k_{i,j}\alpha_i \qquad (17)$$

The kinetic model, including all the species and their oxidation rates, allows us to describe all the observed experimental results. Considering the changes in the Fe(II) speciation due to pH and $[\mathrm{HCO_3^-}]$ variability, the individual rate constants also describe the effect of pH and carbonate levels on the oxidation of Fe(II) at different H_2O_2 concentrations. The contribution of the different Fe(II) species for the oxidation in oxygen saturated seawater at $[\mathrm{H_2O_2}]_o=275$ nM and $[\mathrm{H_2O_2}]_o=50$ nM with $[\mathrm{Fe(II)}]_o=250$ nM are shown in Fig. 10. The hydrolysis Fe(II) species dominate the Fe(II) oxidation process between $\mathrm{pH_F}$ 6 to 8.5. When $[\mathrm{H_2O_2}]_o=275$ nM, the $\mathrm{FeOH^+}$ species dominate and the oxidation rates are independent of the oxygen concentration. Only at a $\mathrm{pH_F}$ over 8 does the $\mathrm{Fe(OH)_2}$ species contribute over 30%, and 40% at the $\mathrm{pH_F}=8.17$. The carbonate species, $\mathrm{Fe(CO_3)_2^{2-}}$, over $\mathrm{pH_F}=8$ contribute 22% to the overall oxidation rate. These results are consistent with the measurements shown in Fig. 9 where the slope is one near a pH of 8. At $[\mathrm{H_2O_2}]_o=$ 50 nM, in the pH range from 6.5 to 7.7, $\mathrm{FeOH^+}$ is the most active species with values over 30% and a maximum contribution at $\mathrm{pH_F}=7$ of 45%. $\mathrm{FeCO_3}$ contributes around 20% at this pH. This is also in accordance with the first-order pH dependence found at this $\mathrm{pH_F}$ range, shown in Fig. 9. The contribution of $\mathrm{Fe(OH)_2}$ becomes important at a pH over 7.7 followed by $\mathrm{Fe(CO_3)_2^{2-}}$ and, according to the results presented in Fig. 9, the change in the pH dependence of the oxidation rate from first to second order is related to the major role of $\mathrm{Fe(OH)_2}$.

Fig. 11 presents the pseudo-first order oxidation rates determined in the pH range 6.5 to 8.5 in oxygen saturated seawater, in nitrogen bubbled seawater (remained $[\mathrm{O_2}]=17$ μM) and seawater with increased concentrations of H_2O_2 (50 nM to 720 nM) at $\mathrm{pH_F}=8.17$ (Table 2). Model predictions determined using the individual rate constants presented in this work (Table 3) are included; they clearly show the excellent agreement between experimental and modeled results. At a fixed pH, the model describes the oxidation rates as a function of increased $[\mathrm{H_2O_2}]$ both at $[\mathrm{Fe(II)}]_o=250$ nM (Fig. 5) and $[\mathrm{Fe(II)}]_o=30$ nM (Fig. 8). These results confirm the applicability of the kinetic model and the corresponding individual oxidation rates at nanomolar levels of Fe(II) under different oxidant conditions found in natural waters. In oceanic surface waters with low $[\mathrm{H_2O_2}]$, the oxidation of Fe(II) is controlled by the dissolved $[\mathrm{O_2}]$ while in coastal surface waters, where the $[\mathrm{H_2O_2}]$ becomes

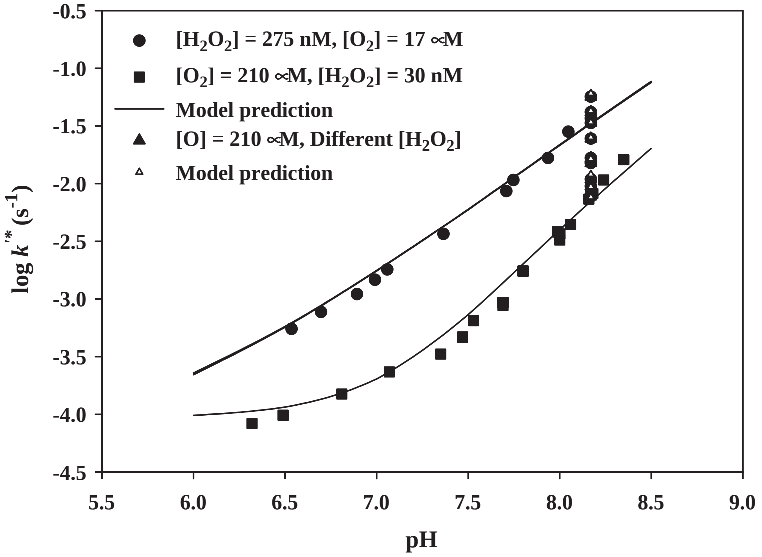

Fig. 11. Pseudo-first order oxidation rate determined in the pH range 6.5 to 8.5 with $[\mathrm{O_2}]=210$ μM (oxygen saturated seawater), $[\mathrm{O_2}]=17$ μM (N_2-bubbled seawater), and oxygen saturated seawater with increased $[\mathrm{H_2O_2}]_o$ at the $\mathrm{pH_F}=8.17$.

over 200 nM, Fe(II) the oxidation can be controlled by H_2O_2 even at high pH. These results should be useful in estimating the rates of oxidation of Fe(II) with O_2, H_2O_2 and their mixtures over a wide range of conditions.

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