Nonlinear dependence of the oxidation rate of Fe(II) on dissolved oxygen under low-O₂ conditions in aqueous solutions

Hirokazu SUGIMORI^{*,**}, Yoshiki KANZAKI^{*}, Kohei YOKOTA^{*,***} and Takashi MURAKAMI^{*}

^{*}Department of Earth and Planetary Science, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

^{**}Present address: Tokyo Metropolitan Industrial Technology Research Institute, 3-13-10 Nishigaoka, Kita-ku, Tokyo 115-8586, Japan

^{***}Present address: NTT DATA Corporation, 3-3-3 Toyosu, Koto-ku, Tokyo 135-6033, Japan

The effect of dissolved O₂ (DO) concentration or partial pressure of atmospheric oxygen (P_{O_2}) on the Fe(II) oxidation rate was investigated at room temperature, by changing pH from 6.89 to 8.03 and P_{O_2} from 7.5×10^{-5} to 0.20 atm. The oxidation experiments were conducted in a glove box into which a gas mixture of Ar and Ar + O₂ (1%) was introduced continuously to maintain a given DO concentration. The DO concentration was changed by varying the mixing ratio of Ar and Ar + O₂ (1%). The decay constant of the oxidation (λ) was estimated from the experimental data, by assuming that the reaction shows pseudo-first-order behavior:

$$-\frac{d[\text{Fe(II)}]}{dt} = \lambda [\text{Fe(II)}] = k [\text{Fe(II)}][\text{O}_2]^x [\text{OH}^-]^y,$$

which indicates λ ($k[\text{O}_2]^x[\text{OH}^-]^y$) depends on the solution pH and DO concentration. After determining the pH dependence of the oxidation rate ($k' = k[\text{OH}^-]^y$), we obtained the relationships between the modified rate constant ($k' = k[\text{O}_2]^x$) and P_{O_2} . The relationships revealed that the oxidation rate deviated from the linear dependence ($x = 1$) at low P_{O_2} ($<10^{-2}$ atm) and that the oxidation proceeded faster than in the case where x was assumed to be 1. Our results implied that the atmospheric O₂ levels (between 2.5 and 2.0 Ga) estimated from the Fe(II) oxidation in paleosols, ancient soils formed by weathering, are overestimated if the x dependence of the oxidation rate is not taken into account.

Keywords: Fe(II) oxidation rate, Low-oxygen, Weathering, Atmospheric oxygen evolution

INTRODUCTION

The Fe redox cycle plays an important role in the geochemical systems in terrestrial and marine environments. The concentration of dissolved Fe in groundwater and seawater is closely related to the behavior of the other transition metals in solution and bioavailability (Stumm and Sulzberger, 1992). The oxidation states of Fe [Fe(0), Fe(II), and Fe(III)] mainly control the concentration of total dissolved Fe in solution. Under natural conditions at the Earth's surface, Fe(II) is relatively soluble and labile,

while Fe(III) preferentially precipitates as oxides/hydroxides.

Fe(II) oxidation is a critical process for Fe behavior in solution. The most accepted mechanisms of Fe(II) oxidation by dissolved O₂ (DO) (e.g., Stumm and Lee, 1961; King et al., 1995; Emmenegger et al., 1998; Santana-Casiano et al., 2005) are as below:

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H. Sugimori, sugimori.hirokazu@iri-tokyo.jp

T. Murakami, murakami@eps.s.u-tokyo.ac.jp Corresponding author

where reactions 1 and/or 3 are the rate-determining steps. The Fe(II) oxidation rate has been intensively studied by numerous researchers (Stumm and Lee, 1961; Singer and Stumm, 1970; Theis and Singer, 1974; Tamura et al., 1976; Tamura et al., 1980; Sung and Morgan, 1980; Lowson, 1982; Davison and Seed, 1983; Millero, 1985; Millero et al., 1987; Liang et al., 1993a; Liang et al., 1993b; King et al., 1995; King, 1998; Emmenegger et al., 1998; Rose and Waite, 2002; Rosso and Morgan, 2002; Pullin and Cabaniss, 2003; González-Dávila et al., 2005; Santana-Casiano et al., 2005; Pham et al., 2006; Pham and Waite, 2008). Stumm and Lee (1961) have established a rate law for Fe(II) oxidation by DO in natural water at pH >5:

$$\frac{-d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}][\text{O}_2][\text{OH}^-]^2 \quad (5),$$

where [Fe(II)], [O₂], and [OH⁻] are the concentrations of total Fe(II), DO, and OH⁻, respectively, in solution (mol L⁻¹), and *k* is the rate constant (L³ mol⁻³ min⁻¹). The DO concentration can be given in terms of partial pressure of atmospheric oxygen (*P*_{O₂}) according to Henry's law, when the solution is in equilibrium with the atmosphere. The Fe(II) oxidation rate is a function of the concentrations of DO and OH⁻. The effects of [OH⁻], which can be substituted by the effects of pH, have been investigated in the range 2 < pH < 9, and the effects of other solution parameters such as temperature, ionic strength, and natural organic matter have been also studied (Singer and Stumm, 1970; Theis and Singer, 1974; Millero et al., 1987; Sung and Morgan, 1980; Pullin and Cabaniss, 2003; Santana-Casiano et al., 2005). Singer and Stumm (1970) have shown that the power of [OH⁻] is smaller than 2 at pH < 5 and that the oxidation rate is independent of pH at pH < 3.5. The effect of DO concentration on the oxidation rate has been investigated at *P*_{O₂} values that are slightly lower and higher than the present atmospheric O₂ level, i.e., 0.107–0.195 atm (Stumm and Lee, 1961) and 0.308–0.903 atm (Tamura et al., 1976), respectively. In these studies, it was concluded that the oxidation rate shows a linear dependence on [O₂]. On the other hand, Liang et al. (1993b) have examined the [O₂] dependence of the Fe(II) oxidation rate under low-O₂ conditions (*P*_{O₂} = 0.005 atm) and indicated that the Fe(II) oxidation rate deviates from the linear dependence on [O₂] at *P*_{O₂} = 0.005 atm.

Thus, the dependence of [O₂] on the Fe(II) oxidation rate under low-O₂ conditions (*P*_{O₂} < 10⁻² atm) has been scarcely studied because of the oxic nature of the present atmosphere and solution. However, low-O₂ conditions must be taken into consideration when investigating the Fe(II) oxidation rate in the Precambrian, especially be-

tween 2.5 and 2.0 Ga in the Paleoproterozoic, where atmospheric oxygen increased dramatically (see recent reviews, Canfield, 2005; Catling and Claire, 2005; Sreenivas and Murakami, 2005; Holland, 2006; Kasting and Ono, 2006; Kump, 2008). Geological records of the mass-independent fractionation of sulfur isotopes suggest that *P*_{O₂} increased from approximately ≤10⁻⁶ atm at 2.45 Ga to ≥10⁻⁶ atm at 2.32 Ga and to ≥10⁻³ atm at 2.0 Ga (Farquhar et al., 2000; Pavlov and Kasting, 2002; Farquhar and Wing, 2003; Bekker et al., 2004). These *P*_{O₂} levels are far lower than those previously used in experiments for determining the Fe(II) oxidation rate. On the other hand, the Fe contents of paleosols, ancient soils formed by weathering, have been widely used to estimate the *P*_{O₂} levels in the Precambrian atmosphere because of the dependence of the Fe(II) oxidation rate on the *P*_{O₂} level (e.g., Holland, 1984; Rye and Holland, 1998). If the Fe(II) oxidation rate deviates from the linear dependence on [O₂] under low-O₂ conditions, the redistribution of Fe between a paleosol and paleogroundwater would be different from that predicted by the classical rate law (equation 5). Murakami et al. (2007) have proposed a method to apply the Fe(II) oxidation kinetics to the Fe(II) and Fe(III) concentrations in paleosols, where they emphasize the importance of the *P*_{O₂} dependence of the Fe(II) oxidation rate which can estimate atmospheric oxygen evolution.

We examined the effect of DO or *P*_{O₂} on the Fe(II) oxidation rate for the DO range 0.0032–8.3 mg L⁻¹, which is equivalent to *P*_{O₂} = 7.5 × 10⁻⁵–0.20 atm. The minimum and maximum values in this range correspond to the Paleoproterozoic and present-day atmospheric *P*_{O₂} levels, respectively. To assess the effect of the DO concentration on the rate law, we modify equation 5 as

$$\frac{-d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}][\text{O}_2]^x[\text{OH}^-]^y \quad (6),$$

where *x* and *y* are variables (0 ≤ *x* ≤ 1 and 0 ≤ *y* ≤ 2) and will be derived from our experiments below. The DO concentrations are controlled by introducing an Ar/O₂ gas mixture in a glove box. The aim of the present study is to demonstrate the nonlinear dependence of the Fe(II) oxidation rate on the DO concentration under low-O₂ conditions.

EXPERIMENTAL METHODS

Reagents

All the stock solutions were prepared using “Milli-Q,” de-ionized water (18.2 MΩ cm). All the chemicals used were reagent-grade: tris(hydroxymethyl)aminomethane

($\text{C}_4\text{H}_{11}\text{NO}_3$; purity >99.9%, Sigma Chemical Co., USA), hydrochloric acid (HCl; assay 35.0–37.0%, Wako Pure Chemical Industries, Ltd., Japan), sodium bicarbonate (NaHCO_3 ; assay 99.5–100.3% after drying, Wako Pure Chemical Industries, Ltd., Japan), sodium hydroxide (NaOH; purity >97.0%, Kanto Chemical Co., Ltd., Japan), Fe(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; purity >99.0%, Kanto Chemical Co., Ltd., Japan), ammonia solution (NH_3 ; assay 25.0–27.9%, Wako Pure Chemical Industries, Ltd., Japan), acetic acid (CH_3COOH ; purity >99.7%, Kanto Chemical Co., Ltd., Japan), and 4-(2-pyridylazo)resorcinol (PAR) ($\text{C}_{11}\text{H}_9\text{N}_3\text{O}_2$; purity >97.0%, Wako Pure Chemical Industries, Ltd., Japan). The purities of Ar, O_2 , and CO_2 gases were >99.99%, >99.95%, and >99.5%, respectively (Suzuki Shokan Co., Ltd., Japan).

Oxidation experiments

Oxidation experiments under low- O_2 conditions ($[\text{O}_2] \leq 0.40 \text{ mg L}^{-1}$) were conducted in a glove box (Sugimori et al., 2009), and similar experiments were performed under the present atmospheric O_2 conditions ($[\text{O}_2] = 8.3 \text{ mg L}^{-1}$) in the ambient atmosphere. Both sets of experiments were carried out at room temperature ($22 \pm 1^\circ\text{C}$). The error of $\pm 1^\circ\text{C}$ gave a difference of ± 0.02 in the value of $\log k$ in equation 5 (Millero et al., 1987). Fe(II) oxidation proceeded in the buffer solution taken in a polypropylene bottle. The solution pH was adjusted in the range 6.9–8.1 with 0.04 M tris(hydroxymethyl)aminomethane and HCl (tris buffer, ionic strength $I = 0.02$ –0.05). All the pH measurements were performed using an F-21 pH meter (Horiba, Japan), calibrating on the free hydrogen scale with pH 6.86 and pH 9.18 buffers at 22°C . The error in the pH value was ± 0.02 . Fe(II) stock solutions (2 and 15 mM) were prepared by dissolving $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 0.01 M HCl solution. An aliquot of the Fe(II) stock solution was delivered to the buffer solution at the start of the oxidation experiment. The pH of the buffer solution remained almost the same as the initial pH, within a variation of ± 0.02 during the experiments. The initial Fe(II) concentrations, $[\text{Fe(II)}]_0$, are given in Table 1.

For the oxidation experiments under low- O_2 conditions, first, the air in the glove box was evacuated by a vacuum pump, and Ar/Ar + O_2 (1%) mixture with a definite mixing ratio was injected. Then, approximately 100 mL of the buffer solution was bubbled with the gas mixture in order to exchange the dissolved gas species in the solution. This process filled the glove box with the gas that was blown out from the solution. The concentration of DO in the buffer solution equilibrated with the atmosphere in the glove box was monitored by a DO meter (Toko Chemical Laboratories DO Meter TOX-02H; de-

tection limit: 0.02 ppb) placed in the glove box. When the DO concentration reached the expected value, $\sim 0.5 \text{ mL}$ of the Fe(II) stock solution was added to the buffer solution (100 mL for the total volume). The solution was bubbled with the gas mixture (flow rate: 200–550 mL min^{-1} depending on DO) throughout the experiment, and the DO concentration was monitored during the entire experiment. The change in the DO concentration during the experiment was 1–9% (the change became larger with a decrease in the DO concentration; see Table 1); this difference, however, does not affect the discussion below. The DO concentration was controlled by altering the mixing ratio of Ar and Ar + O_2 (1%) in the input gas and was in the range 0.0032 – 0.40 mg L^{-1} , corresponding to a P_{O_2} range of 7.5×10^{-5} to $9.4 \times 10^{-3} \text{ atm}$. For the experiments under the present atmospheric O_2 conditions, 100 mL of the buffer solution was kept in the air until it was equilibrated with the present P_{O_2} condition ($[\text{O}_2] = 8.3 \text{ mg L}^{-1}$, equivalent to $P_{\text{O}_2} = 0.20 \text{ atm}$). 7 mL of the solution sample was collected in a polypropylene bottle once during a given period for analysis. A solution of 1 mol L^{-1} HCl was added to the bottle to lower the pH and prevent further oxidation of Fe(II).

All the experimental conditions are shown in Table 1. The DO concentrations were set to 8.3, 0.40, 0.039, and 0.0032 mg L^{-1} , corresponding to experimental runs 1, 2, 3, and 4, respectively. The pH values of the buffer solutions were adjusted to 6.89, 7.43, 7.69, and 8.03, corresponding to N, M, A, and S, respectively, for the four experimental runs. Experiments with different initial concentrations of Fe(II) were conducted at various P_{O_2} and pH values to examine the effect of the total Fe(II) concentration on the oxidation rate (labeled with L). Two of the experiments (3AL and 3SL in Table 1) were performed at slightly different values of DO and pH from those mentioned above. Two additional oxidation experiments were also carried out to investigate the effects of P_{O_2} and buffer solution on the oxidation ($[\text{O}_2] = 0.051 \pm 0.003 \text{ mg L}^{-1}$ and $0.110 \pm 0.005 \text{ mg L}^{-1}$, corresponding to runs 5A and 6A, respectively, in Table 1). For runs 5A and 6A, the solution pH was buffered with a $\text{CO}_2/\text{HCO}_3^-$ solution (3% CO_2 gas flowing with Ar and O_2 , and 9 mM NaHCO_3) (e.g., Millero et al., 1987) and adjusted to 7.66 ± 0.02 with 1 mol L^{-1} NaOH ($I = 0.013$). Under low- O_2 conditions, all the experiments, from bubbling with the gas mixture to solution sampling, were carried out in the glove box. The reaction duration and the number of samplings were 4–14,000 min and 7–12, respectively (see Fig. 1 for details).

Fe concentration analysis

The dissolved Fe(II) and Fe(III) in the collected solution

Table 1. Summary of the experimental conditions and the rate constants of Fe(II) oxidation

Run number	[O ₂], mg L ⁻¹	P _{O₂} ^a , atm	pH	[Fe(II)] ₀ , mg L ⁻¹	Ionic strength, mol L ⁻¹	log λ ^b , min ⁻¹	log k _{app} ^c	log k'' ^d	log k' ^e
1N	8.3 (0.1) ^f	2.0 × 10 ⁻¹	6.89 (0.02)	0.42 (0.03)	0.040 (0.001)	-2.72 (0.02)	15.08 (0.04)	0.87 (0.02)	11.49 (0.05)
1M	8.3 (0.1)	2.0 × 10 ⁻¹	7.43 (0.02)	0.43 (0.03)	0.035 (0.001)	-1.23 (0.09)	15.49 (0.09)	2.35 (0.09)	11.90 (0.10)
1A	8.3 (0.1)	2.0 × 10 ⁻¹	7.69 (0.02)	0.50 (0.04)	0.031 (0.001)	-0.59 (0.04)	15.61 (0.05)	3.00 (0.04)	12.02 (0.06)
1NL	8.3 (0.1)	2.0 × 10 ⁻¹	6.89 (0.02)	4.5 (0.5)	0.040 (0.001)	-2.71 (0.03)	15.09 (0.04)	0.88 (0.03)	11.50 (0.05)
1ML	8.3 (0.1)	2.0 × 10 ⁻¹	7.43 (0.02)	4.1 (0.4)	0.035 (0.001)	-1.24 (0.01)	15.48 (0.03)	2.34 (0.01)	11.89 (0.05)
1AL	8.3 (0.1)	2.0 × 10 ⁻¹	7.69 (0.02)	4.0 (0.4)	0.031 (0.001)	-0.55 (0.02)	15.65 (0.04)	3.03 (0.02)	12.06 (0.05)
2N	0.40 (0.02)	9.4 × 10 ⁻³	6.89 (0.02)	0.37 (0.03)	0.040 (0.001)	-3.54 (0.02)	15.58 (0.04)	1.36 (0.03)	10.67 (0.05)
2M	0.40 (0.02)	9.4 × 10 ⁻³	7.43 (0.02)	0.41 (0.03)	0.035 (0.001)	-2.50 (0.04)	15.54 (0.05)	2.40 (0.04)	10.63 (0.06)
2A	0.40 (0.02)	9.4 × 10 ⁻³	7.69 (0.02)	0.43 (0.03)	0.031 (0.001)	-1.93 (0.03)	15.58 (0.05)	2.97 (0.04)	10.68 (0.06)
2NL	0.40 (0.02)	9.4 × 10 ⁻³	6.89 (0.02)	3.8 (0.4)	0.040 (0.001)	-3.60 (0.02)	15.52 (0.04)	1.30 (0.03)	10.61 (0.05)
2AL	0.40 (0.02)	9.4 × 10 ⁻³	7.69 (0.02)	3.5 (0.4)	0.031 (0.001)	-1.86 (0.04)	15.65 (0.05)	3.04 (0.04)	10.75 (0.06)
3N	0.039 (0.003)	9.2 × 10 ⁻⁴	6.89 (0.02)	0.43 (0.03)	0.040 (0.001)	-4.20 (0.05)	15.93 (0.07)	1.71 (0.06)	10.01 (0.07)
3M	0.039 (0.003)	9.2 × 10 ⁻⁴	7.43 (0.02)	0.41 (0.03)	0.035 (0.001)	-3.17 (0.06)	15.88 (0.08)	2.75 (0.07)	9.96 (0.08)
3A	0.039 (0.003)	9.2 × 10 ⁻⁴	7.69 (0.02)	0.41 (0.03)	0.031 (0.001)	-2.59 (0.04)	15.93 (0.06)	3.32 (0.06)	10.02 (0.06)
3S	0.039 (0.003)	9.2 × 10 ⁻⁴	8.03 (0.02)	0.44 (0.03)	0.022 (0.002)	-1.89 (0.08)	15.95 (0.09)	4.02 (0.09)	10.04 (0.09)
3AL	0.038 (0.003)	8.9 × 10 ⁻⁴	7.74 (0.02)	4.5 (0.1)	0.051 (0.005)	-2.61 (0.03)	15.85 (0.07)	3.32 (0.07)	9.90 (0.05)
3SL	0.038 (0.003)	8.9 × 10 ⁻⁴	8.12 (0.02)	4.1 (0.6)	0.034 (0.004)	-1.78 (0.05)	15.91 (0.06)	4.14 (0.07)	9.97 (0.07)
4A	0.0032 (0.0003)	7.5 × 10 ⁻⁵	7.69 (0.02)	0.43 (0.03)	0.031 (0.001)	NA ^g			
4S	0.0032 (0.0003)	7.5 × 10 ⁻⁵	8.03 (0.02)	0.41 (0.03)	0.022 (0.002)	NA			
4SL	0.0032 (0.0003)	7.5 × 10 ⁻⁵	8.03 (0.02)	3.4 (0.3)	0.022 (0.002)	NA			
5A ^h	0.051 (0.003)	1.3 × 10 ⁻³	7.66 (0.02)	0.45 (0.03)	0.013 (0.001)	-2.61 (0.01)	15.86 (0.04)	3.19 (0.03)	10.06 (0.05)
6A ^h	0.110 (0.005)	2.8 × 10 ⁻³	7.66 (0.02)	0.46 (0.03)	0.013 (0.001)	-2.38 (0.02)	15.76 (0.04)	3.09 (0.03)	10.29 (0.05)

^a Conversion of [O₂] according to Henry's law at 22 °C.^b λ was obtained from the data in Figure 1 assuming pseudo-first-order dependence.^c k_{app} was obtained from λ, [O₂], and [OH⁻] in the table according to λ = k_{app} [O₂] [OH⁻]².^d k'' was obtained from λ and [O₂] in the table according to λ = k'' [O₂].^e k' was obtained from λ and [OH⁻] in the table according to λ = k' [OH⁻]².^f Figure in parentheses denotes uncertainty or expanded uncertainty.^g Not available because of no pseudo-first-order dependence (see RESULTS).^h CO₂/HCO₃⁻ buffer was used.

Figure 1. Observed Fe(II) concentrations as a function of time at P_{O_2} values of (a) 0.20, (b) 9.4×10^{-3} , (c) 9.2×10^{-4} , and (d) 7.5×10^{-5} atm, and (e) for the experiments with $\text{CO}_2/\text{HCO}_3^-$ buffer solution. The dotted curve in (d) demonstrates obvious deviation from first-order behavior. See Table 1 for the run numbers given in the figure. The λ values in Table 1 are obtained from linear regressions of the $\text{Ln}[\text{Fe(II)}/\text{Fe(II)}_0]$ values, assuming pseudo-first-order behavior. The upper horizontal axes should be used for runs 1N, 1NL, 2N, 2NL, 3N, 3M, and 4A.

were separated using high-pressure liquid chromatography (pumps, JASCO 880-PU and Shimadzu LC-10Ai; column, Shim-pack IC-C1; and detector, Shiseido Nanoscope SI-1). Then, the collected solution was mixed with 4-(2-pyridylazo)resorcinol (PAR) solution, which was prepared using 0.2 mM PAR, 3 M NH₃ solution, and 1 M CH₃COOH, to form an Fe(II)-PAR complex (Roston, 1984). Finally, the concentration of Fe(II) in the collected solution was measured by spectrophotometry (Nanoscope SI-1) at 520 nm of absorbance; the detection limit of the Fe(II) concentration in the solution in this case was about 0.02 mg L⁻¹.

RESULTS

The rate law for Fe(II) oxidation (equation 6) reduces to a pseudo-first-order equation:

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

where

$$\lambda = k[\text{O}_2]^x[\text{OH}^-]^y \quad (8).$$

Equation 7 is then integrated to

$$\ln \frac{[\text{Fe(II)}]}{[\text{Fe(II)}]_0} = -\lambda t \quad (9),$$

where $[\text{Fe(II)}]_0$ is the initial Fe(II) concentration (mol L⁻¹), and t is the elapsed time (min). Then, the value of λ (min⁻¹) will be obtained from the slope of $\ln([\text{Fe(II)}]/[\text{Fe(II)}]_0)$ variation against time.

Figure 1 shows the plots of $\ln([\text{Fe(II)}]/[\text{Fe(II)}]_0)$ against time for all the oxidation experiments. The Fe(II) oxidation rates or the λ values changed with pH and $[\text{O}_2]$ (Table 1). Pseudo-first-order behavior was observed in all runs except for runs 4A, 4S, and 4SL at $P_{\text{O}_2} = 7.5 \times 10^{-5}$ atm, as discussed in detail below. Linear regression with correlation coefficient (R^2) values of more than 0.99 was observed in all the runs except for runs 1M ($R^2 = 0.98$) and 3M and 3S ($R^2 = 0.97$). The last couple of data points for runs 2A and 2M deviated slightly from linearity (Fig. 1b). Although $[\text{O}_2]$ was not in excess of $[\text{Fe(II)}]_0$ for runs 3AL and 3SL, a linear relationship was observed between $\ln([\text{Fe(II)}]/[\text{Fe(II)}]_0)$ and time (Fig. 1c). Note that the solutions were bubbled with the gas mixture throughout the course of the experiments, as mentioned above. The experiments performed for $[\text{O}_2] = 8.3, 0.4$, and 0.04 mg L⁻¹ revealed that the difference in the initial Fe(II) concentration had little effect on λ (runs 1N/1NL, 1M/1ML,

1A/1AL, 2N/2NL, 2A/2AL, 3A/3AL, and 3S/3SL in Table 1 and solid/open symbols in Figs. 1a, 1b, and 1c).

The oxidation rates apparently became faster in the later stages of the reactions, and pseudo-first-order behavior was not observed at $P_{\text{O}_2} = 7.5 \times 10^{-5}$ atm (equivalent to $[\text{O}_2] = 0.0032$ mg L⁻¹) (Fig. 1d). The values of λ were estimated from the slopes by fitting the first three data points, including those at time $t = 0$, for runs 4A, 4S, and 4SL ($\log \lambda = -4.27, -3.41$, and -3.80 , respectively). The difference in the initial Fe(II) concentration had little effect on λ , as revealed by the experiments performed at $P_{\text{O}_2} = 0.20, 9.4 \times 10^{-3}$, and 9.2×10^{-4} atm (Figs. 1a, 1b and 1c). However, the oxidation rate for run 4SL ($[\text{Fe(II)}]_0 = 3.4$ mg L⁻¹; pH = 8.03) was slightly slower than that for run 4S ($[\text{Fe(II)}]_0 = 0.41$ mg L⁻¹; pH = 8.03) in the earlier stages of the reactions (Fig. 1d). The initial concentrations of Fe(II) (0.41 – 3.4 mg L⁻¹, equivalent to 7.3×10^{-6} – 6.1×10^{-5} mol L⁻¹) were higher than the DO concentration (0.0032 mg L⁻¹, equivalent to 1.0×10^{-7} mol L⁻¹) (Table 1). Although DO was supplied to the buffer solution by continuous bubbling of the input gas, the rate of DO consumption by Fe(II) oxidation could be faster than that of O₂ supply to the solution, and the actual DO concentration in the exact reaction area was probably lower than 0.0032 mg L⁻¹ (runs 4A, 4S, and 4SL). This explains why the apparent oxidation rate at a higher initial concentration of Fe(II) is slower than that at a lower Fe(II) concentration at $P_{\text{O}_2} = 7.5 \times 10^{-5}$ atm (runs 4S and 4SL in Fig. 1d) and why the oxidation rate is generally slow when the concentration of O₂ is lesser than that of Fe(II).

DISCUSSION

Effect of H₂O₂ on the oxidation rate under low-O₂ conditions

Before estimating the pH and P_{O_2} dependence on the Fe(II) oxidation rate, we considered the effect of H₂O₂ on x under low-O₂ conditions, because Fe(II) oxidation by H₂O₂ can affect the oxidation rate (Miller and Sotolongo, 1989; Miller et al., 1991; King et al., 1995; King and Farlow, 2000; González-Dávila et al., 2005; Santana-Casiano et al., 2005; Santana-Casiano et al., 2006), especially at high pH (e.g., pH 8, Pham and Waite, 2008). The H₂O₂ concentration is ~100 nM in modern seawater and is mainly generated through the photooxidation of organic matter (e.g., Zika et al., 1985). However, we assumed that H₂O₂ is generated only by reaction 2 because in the present study, we considered the Fe(II) oxidation in weathering during the Paleoproterozoic, when there was little or no life activity on land. Assuming that reactions 2 and 4 are fast and stoichiometric with respect to Fe(II), the rate

of change of Fe(II) and H₂O₂ is described by equations 10 and 11, respectively (King et al., 1995):

$$\frac{d[\text{Fe(II)}]}{dt} = -2k_1 [\text{Fe(II)}][\text{O}_2] - 2k_3 [\text{Fe(II)}][\text{H}_2\text{O}_2] \quad (10)$$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_1 [\text{Fe(II)}][\text{O}_2] - k_3 [\text{Fe(II)}][\text{H}_2\text{O}_2] \quad (11),$$

where k_1 and k_3 are the rate constants of reactions 1 and 3, respectively, and depend on pH. k_1 and k_3 were obtained from Table 1 in King et al. (1995). For the calculations, we assumed that the temperature and pH were 25 °C and 8.0, respectively. The changes in [Fe(II)] with time were calculated using the Runge-Kutta method for P_{O_2} values of 0.2, 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5} atm and [Fe(II)]₀ values of 7.2×10^{-5} and 7.2×10^{-6} mol L⁻¹ (micromolar levels; 4.0 and 0.4 mg L⁻¹, respectively, similar to the present experimental [Fe(II)]₀ in Table 1) from equations 10 and 11, and for [Fe(II)]₀ = 1.0×10^{-7} mol L⁻¹ (nanomolar level) for comparison. Using the classical rate law (equation 5), λ ($= k[\text{O}_2][\text{OH}^-]^2$) values were calculated from the $\ln([\text{Fe(II)}]/[\text{Fe(II)}]_0)$ vs. time relationships for the above conditions.

If the Fe(II) oxidation by H₂O₂ has an influence on x , the $\log \lambda$ values calculated using equations 10 and 11 deviate from the linear dependence of $\log(P_{\text{O}_2})$ at low O₂. The calculations have revealed that the linear relationship between $\log \lambda$ and $\log(P_{\text{O}_2})$ is retained at micromolar levels of [Fe(II)]₀ (circles and diamonds in Fig. 2), clearly indicating that there is no effect of H₂O₂ on the x variation. At nanomolar levels of [Fe(II)]₀ (crosses in Fig. 2), the relationship between λ and P_{O_2} is the same as those at micromolar levels of [Fe(II)]₀ at low P_{O_2} , whereas the oxidation rates are slightly lower at high P_{O_2} . The slightly higher oxidation rates at micromolar levels at high pH and P_{O_2} have been explained by the rapid formation of H₂O₂ (Santana-Casiano et al., 2005), in addition to the autocatalysis of Fe(II) oxidation due to the presence of Fe oxyhydroxides (Pham and Waite, 2008). The linear relation between $\log \lambda$ and $\log(P_{\text{O}_2})$ indicates that there is no effect of H₂O₂ on the x variation at micromolar levels of [Fe(II)]₀ and even at nanomolar levels, at low P_{O_2} . Therefore, we exclude the effect of H₂O₂ on the x variation from further discussion.

Estimation of power y and assessment of the λ values

Table 1 gives the values of k_{app} calculated from $\lambda = k_{\text{app}} [\text{O}_2][\text{OH}^-]^2$ according to the classical oxidation rate law (equation 5). The values of k_{app} vary significantly, which can be explained by k in equation 6, but not by k in equa-

Figure 2. The relationships between λ and P_{O_2} calculated on the basis of equations 10 and 11 for [Fe(II)]₀ = 7.2×10^{-5} , 7.2×10^{-6} , and 1.0×10^{-7} mol L⁻¹ (circles, diamonds, and crosses, respectively) considering the effect of H₂O₂. The solid line with a slope of 1 demonstrates the linear dependence of $\log \lambda$ on $\log(P_{\text{O}_2})$. See text for the explanation.

tion 5 ($\log k = 21.56 - 1545/T - 3.29I^{0.5} + 1.52I$, given by Millero et al., 1987). To examine the x variation, we have to estimate the y value first. The y value determined here does not affect the x variation.

To estimate the influence of pH on the Fe(II) oxidation rate independently, λ is rewritten as

$$\lambda = k''[\text{O}_2] \quad (12),$$

where $k'' = k[\text{OH}^-]^y$. k'' includes the P_{O_2} effect because $x = 1$ is assumed in equation 12. The values of k'' presented in Table 1 were directly calculated from λ and $[\text{O}_2]$, also given in Table 1. Figure 3 shows the k'' variations plotted against pH for the oxidation experiments performed at P_{O_2} values of 0.20, 9.4×10^{-3} , and 9.2×10^{-4} atm (diamonds, circles, and open triangles, respectively) and for the oxidation experiment performed by Millero et al. (1987) in 9 mM NaHCO₃ solution at 25 °C (crosses). A regression line is drawn in Figure 3 for each data set. The slopes of the regression lines are equivalent to the corresponding y values, as seen from the equation, $k'' = k[\text{OH}^-]^y$. The solid line in Figure 3 is drawn on the basis of the classical oxidation rate law (equation 5) according to the model calculation by Millero et al. (1987); the present experimental conditions, $T = 22$ °C, $I = 0.035$, and $y = 2$, were used for the calculation. The y value obtained from the slope of the k'' variation against pH is ~ 2.1 and 2.0 at P_{O_2} values of 9.4

Figure 3. Rate constant, k'' , as a function of pH ($k'' = k[OH]^y$) at different P_{O_2} levels, along with those reported by Millero et al. (1987). The broken lines are regression lines for the different data sets, and the solid line is the model calculation suggested by Millero et al. (1987) assuming $y = 2$. The numbers in the figure represent values of the slopes of the regression lines. Uncertainties are approximately within the size of the symbols used in the figure. See Table 1 for the exact uncertainties. The data points for runs 3AL and 3SL are not included because their experimental conditions are slightly different from those in the other three series (Table 1). The data points for runs 5A (P_{O_2} : 1.3×10^{-3} atm) and 6A (P_{O_2} : 2.8×10^{-3} atm) are indicated by reverse solid triangles.

$\times 10^{-3}$ and 9.2×10^{-4} atm, respectively, while it is ~ 2.7 at $P_{O_2} = 0.20$ atm, which should be compared to $y = 2$ in the model calculation (Fig. 3). The y value obtained from the experimental data provided by Millero et al. (1987) is also larger than 2 (~ 2.4) in the pH range 6.5–8.

The back-reaction of Fe(III) with superoxide, O_2^- , to form Fe(II) (reaction 1) slows the apparent oxidation rate. Although the back-reaction is not significant at $pH > 7.7$ at micromolar levels of Fe(II) (Santana-Casiano et al., 2005), it is significant at nanomolar levels (Rose and Waite, 2002). The y value is relatively large, ~ 2.7 , at $P_{O_2} = 0.20$ atm, because the oxidation rates or the k'' values are relatively small at $pH = 6.89$ and $P_{O_2} = 0.20$ atm (runs 1N and 1NL in Table 1). Because Fe(III) is relatively soluble at lower pH, the k'' values at $pH = 6.89$ and $P_{O_2} = 0.20$ atm are considered to be affected by the back-reaction of Fe(III). Indeed, the k'' values are smaller than those at $P_{O_2} = 9.4 \times 10^{-3}$ atm and the same pH, although they are similar for $P_{O_2} = 0.20$ and 9.4×10^{-3} atm at higher pH (Fig. 3). In contrast, the effect of the back-reaction of Fe(III) with

O_2^- on the retardation of the Fe(II) oxidation at $pH = 6.89$ under lower- O_2 conditions (runs 2N, 2NL, and 3N in Table 1 and Fig. 3) is not observed. Because the oxidation rates are slower under lower- O_2 conditions, the rates of Fe(III) hydrolysis and precipitation are sufficiently faster than the oxidation rate, and Fe(III) cannot compete with Fe(II) for O_2^- in the solution (reaction 2). Therefore, we ignore the y value at $P_{O_2} = 0.20$ atm. The value 2 for the power of $[OH^-]$ in equation 6, the same value given by the classical rate law (equation 5), is used for further discussions. The y value itself does not affect the discussion in the next section.

Under all O_2 conditions, the values of $\log k''$ are smaller than those given by Millero et al. (1987). Millero et al. (1987) have suggested that the oxidation rate estimated using a tris buffer, as in the present study, is slower than that estimated using a CO_2/HCO_3^- buffer. The data points for the two runs with CO_2/HCO_3^- buffer at $P_{O_2} = 1.3 \times 10^{-3}$ and 2.8×10^{-3} atm are located between those for the runs at $P_{O_2} = 9.4 \times 10^{-3}$ and 9.2×10^{-4} atm at $pH \approx 7.7$ (reverse solid triangles in Fig. 3), indicating the insignificant effect of the buffer solution on the Fe(II) oxidation at low P_{O_2} .

Estimation of power x and implication for Fe behavior in Paleoproterozoic weathering

To estimate the influence of DO or P_{O_2} on the Fe(II) oxidation rate independently, λ is rewritten as

$$\lambda = k'[OH]^2 \quad (13),$$

where $k' = k[O_2]^x$, from which we can know how x varies with $[O_2]$. The values of k' were calculated from λ and $[OH^-]$, which are given in Table 1. Figure 4 shows the k' variation plotted against P_{O_2} . A straight line with a slope of 1 (i.e., $x = 1$) and an intercept of the average of the data at $P_{O_2} = 0.20$ atm is also drawn in Figure 4. The k' values at $pH = 6.89$ and $P_{O_2} = 0.20$ atm (runs 1N and 1NL) are excluded from this figure because of the effect of the retardation mechanism discussed above. The oxidation rates show nearly first-order behavior at $P_{O_2} > 10^{-2}$ atm. Our results clearly show the non-linear dependence of the reaction rate on $[O_2]$ at $P_{O_2} = 9.2 \times 10^{-4}$ atm. Consequently, the Fe(II) oxidation rate deviates from the linear dependence on $[O_2]$ at $P_{O_2} < 10^{-2}$ atm. We speculate that x , the power of $[O_2]$ in equation 6, decreases as P_{O_2} decreases. This trend does not change even if y , the power of $[OH^-]$ in equation 13, changes from 2 to, for instance, 2.6, because x is obtained from the slope at a given P_{O_2} . Liang et al. (1993b) have reported the deviation from the linear dependence at $P_{O_2} = 5 \times 10^{-3}$ atm [$\log(P_{O_2}) = -2.3$]. However,

Figure 4. Rate constant, k' , as a function of P_{O_2} ($k' = k[O_2]^x$) at different pH values, showing the effect of P_{O_2} on the Fe(II) oxidation rate at neutral pH and room temperature. The solid line assumes $x = 1$ with an intercept of the data at $P_{O_2} = 0.20$ atm. Uncertainties are approximately within the size of the symbols used. See Table 1 for the exact uncertainties.

er, their data implies $x > 1$, which is inconsistent with our results. This may be partly because they estimated the rate constants on the basis of the oxidation reactions, which are not first-order reactions.

The first irreversible oxygen rise in the Earth's history (named as the Great Oxidation Event by Holland (2002)) took place between 2.5 and 2.0 Ga, where P_{O_2} increased from $<10^{-6}$ atm at 2.5 Ga to $>10^{-3}$ atm at 2.0 Ga (Farquhar and Wing, 2003). Paleosols have been widely used to estimate O_2 concentrations in the Precambrian atmosphere, and Fe is a major indicator of the oxidation states of paleosols (e.g., Holland, 1984; Rye and Holland, 1998). However, the dependence of x on P_{O_2} has never been taken into account for such estimations. The present results indicate that the oxidation rate of Fe(II) is faster than that predicted from the classical rate law (equation 5, i.e., $x = 1$) at $P_{O_2} < 10^{-2}$ atm. Although our study cannot reveal the Fe(II) oxidation rate at $P_{O_2} < \sim 10^{-4}$ atm, the present results imply that the amount of Fe(III) produced by Fe(II) oxidation (the produced Fe(III) forms Fe(III) (hydr) oxides and remains in a paleosol) is larger at low P_{O_2} than that previously thought. Therefore, the atmospheric oxy-

gen levels between 2.5 and 2.0 Ga are overestimated if the x dependence on P_{O_2} at low P_{O_2} is not taken into account. Thus, estimation of the oxidation states of paleosols without considering the effect of x leads to incorrect estimation of the atmospheric O_2 levels. Although it is impossible to estimate the O_2 levels between 2.5 and 2.0 Ga from the present study alone, the Fe(II) rate law at low P_{O_2} can be used to estimate the O_2 levels during the early Proterozoic, when the rate law is applied to the Fe(II)/Fe(III) concentration ratios in paleosols.

CONCLUSIONS

Although there have been numerous studies on the pH dependence of the Fe(II) oxidation rate, very few studies have reported the DO dependence of the oxidation rate. An in-depth understanding of the DO dependence of the oxidation rate under low- O_2 conditions is important because the P_{O_2} levels in the Paleoproterozoic ($P_{O_2} < 10^{-2}$ atm) have been estimated on the basis of the Fe concentrations in paleosols. We have shown that the Fe(II) oxidation rate deviates from the linear dependence on $[O_2]$ and is higher at $P_{O_2} < 10^{-2}$ atm than that previously thought. The power of $[O_2]$, x , in the rate law probably depends on P_{O_2} at low P_{O_2} . Although the exact relation of x to P_{O_2} could not be clarified, we inferred that x is approximately 1 at $P_{O_2} = 0.20$ atm and decreases with a decrease in P_{O_2} . The present results will give a deeper insight into the Fe behavior during Precambrian weathering and thus help clarify atmospheric oxygen evolution. The oxidation rate of Fe(II) is faster than that predicted from the classical rate law (equation 5) at $P_{O_2} < 10^{-2}$ atm. Consequently, the atmospheric O_2 levels between 2.5 and 2.0 Ga ($P_{O_2} < 10^{-2}$ atm) are overestimated if the O_2 levels are estimated from Fe(II) oxidation in paleosols without considering the x dependence at low P_{O_2} . Further experiments will be required to understand the x dependence at $P_{O_2} < 10^{-4}$ atm because the P_{O_2} level is considered to have increased between 2.5 and 2.0 Ga from $<10^{-6}$ atm (e.g., Farquhar and Wing, 2003).

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