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Ferrous iron oxidation under very low O₂ conditions: Rates, mechanisms and application

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Although there have been numerous studies on Fe(II) oxidation kinetics, few have paid attention to the kinetics under very low O₂ conditions. The importance of Fe(II) oxidation under very low O₂ conditions has been recognized recently; Fe(II) oxidation kinetics has been shown to be applied to the Fe(II)/Fe(III) compositions of paleosols, ancient soils formed by weathering, which can give a quantitative pattern of atmospheric oxygen increase during the Paleoproterozoic (from < 10⁻⁶ atm to > 10⁻³ atm of partial pressure of atmospheric oxygen, pO₂). The effects of pO₂ on Fe(II) oxidation rate was investigated to establish Fe(II) oxidation rate-pO₂ relationship under very low O₂ conditions. All oxidation experiments were carried out in a glove box by introducing Ar gas under conditions of 10⁻³ - 10⁻⁵ atm of pO₂ and 7.57 - 8.12 of pH at room temperature. Because of very low concentrations of Fe(II) (down to ~ 0.1 ppb), new methods were developed to measure Fe(II) concentrations. The dominant species related to oxidation in the pH range examined is suggested to be Fe(OH)₂. The rate law changes from $d[Fe^{2+}]/dt = -k'_{0-high} [Fe(II)][OH^-]^{2.0}[O_2]^{1.0}$ to $-k'_{0-low} [Fe(II)][OH^-]^{2.0} [O_2]^{0.5}$ (k'_0 , the rate constant; [O₂], the concentration of dissolved oxygen) at 0.2 - 0.005 and < 0.005 atm of pO₂, respectively. The former rate law is explained by well-known mechanisms of the four-step reactions. The latter law is established for the first time, where the Fe(II) oxidation rate is faster than that predicted by the classical rate law. To explain the mechanisms, it is suggested that reactions where oxygen produces radicals and hydrogen peroxide play a critical role in addition to the four-step reactions. Such a reaction occurs due to dilute nature of the solutions of ~ 5 - 0.5 ppb of [O₂] and ~ 10 - 0.1 ppb of [Fe(II)], and therefore, will have impact on red-ox chemistry in very dilute solutions. Application of this new oxidation rate law to Fe(II)/Fe(III) ratios of paleosols gives a new quantitative pattern of atmospheric oxygen evolution between 2.5 and 2.0 Ga; atmospheric oxygen evolved rapidly from very low O₂ levels (pO₂ < 10⁻⁶ atm) to ~10⁻⁶ atm of pO₂ at ~ 2.45 Ga and then gradually increased to 10⁻³ atm of pO₂ at 2.0 Ga. Although the constraints set by geological records such as mass independent fractionation of sulfur (i.e., < 10⁻⁶ atm prior to ~ 2.45 Ga, > 10⁻⁶ atm at 2.32 Ga and > 10⁻³ atm at < 2.0 Ga) were not used for the calculations, the atmospheric oxygen evolution model proposed here is consistent with these constraints.

Keywords: Fe(II) oxidation rate, low oxygen, weathering, atmospheric oxygen evolution