

## **Supporting Information**

**to accompany manuscript es051622t entitled**

### **Superoxide-mediated reduction of amorphous ferric oxyhydroxide in seawater**

Manabu Fujii<sup>1\*</sup>, Andrew L. Rose<sup>2</sup>, T. David Waite<sup>2</sup>, Tatsuo Omura<sup>1</sup>

*<sup>1</sup>Department of Civil Engineering, Graduate School of Engineering,*

*Tohoku University, Aoba-yama 6-6-06, Sendai, 980-8579, Japan*

*<sup>2</sup>School of Civil and Environmental Engineering, The University of New South Wales,*

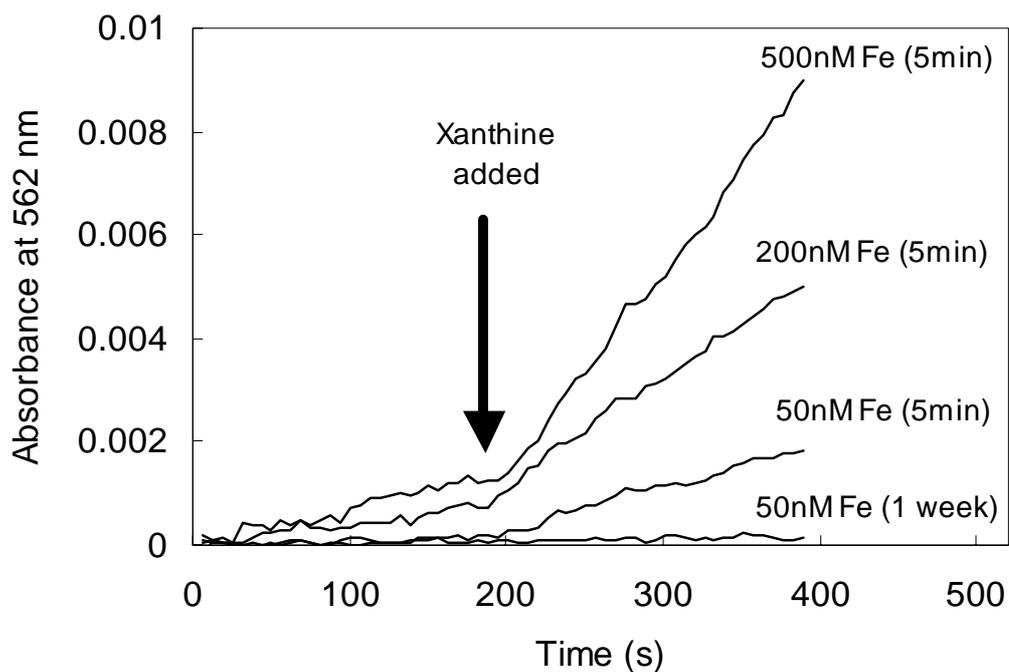
*Sydney, NSW 2052, Australia*

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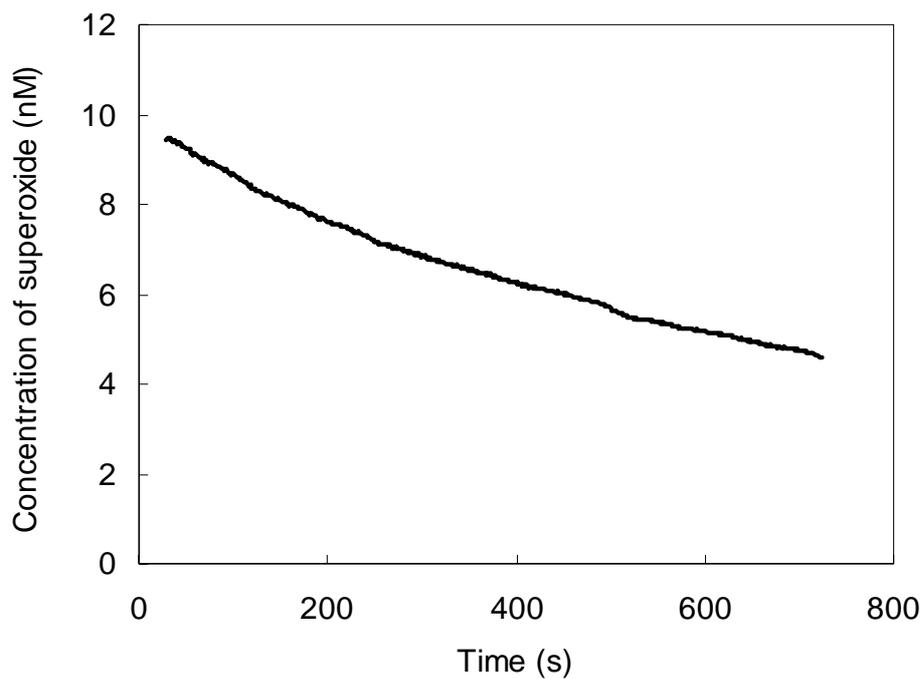
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\*Corresponding author: Phone +81-22-795-7483, FAX +81-22-795-7482, Email  
manabu@water.civil.tohoku.ac.jp

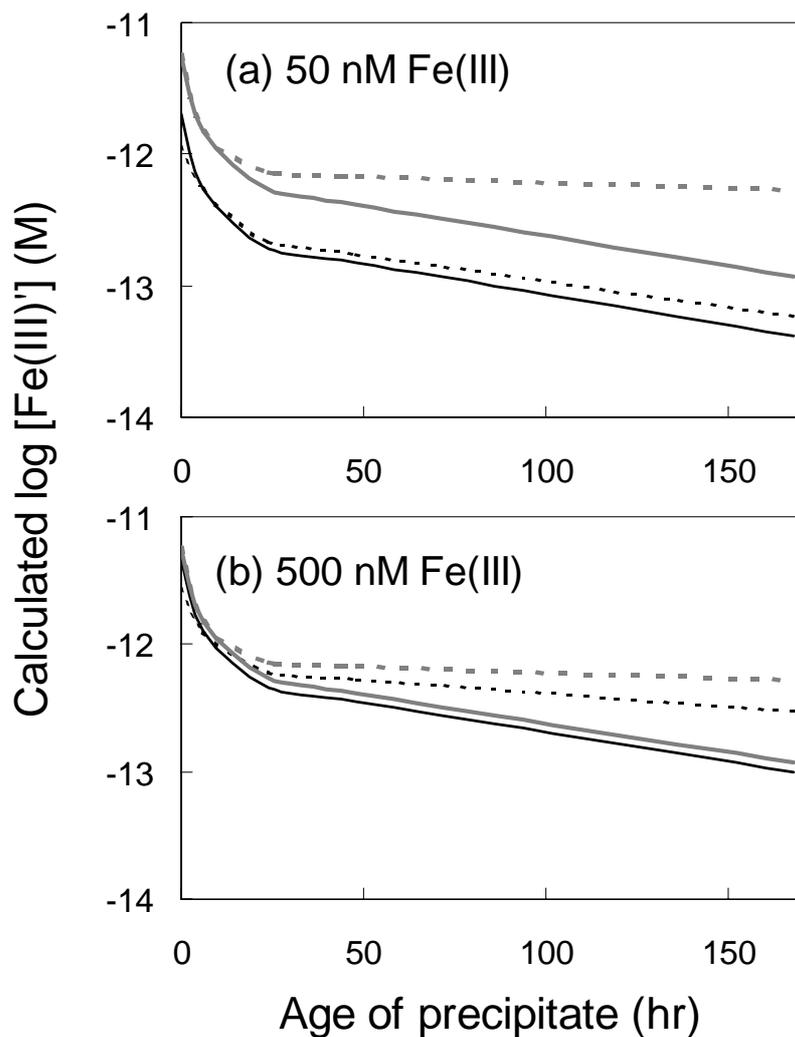
This Supporting Information provides primary kinetic data for superoxide-mediated Fe(II)FZ<sub>3</sub> production rate from amorphous ferric oxyhydroxide (AFO) in seawater (Figure S1), primary kinetic data for bimolecular dismutation rate of superoxide in seawater (Figure S2), and calculated solubility of Fe(III)' in seawater with and without superoxide and ferrozine (Figure S3).



**Figure S1.** Time-dependent production of ferrous-ferrozine complex ( $\text{Fe(II)FZ}_3$ ) from superoxide-mediated dissolution of amorphous ferric oxyhydroxide (AFO) in seawater (pH 8.2). Typical primary kinetic data (50, 200 and 500 nM  $\text{Fe(III)}$  solutions aged for 5 mins and 50 nM  $\text{Fe(III)}$  solution aged for 1 week) are shown. The data are the average of triplicate experiments. In the calculation of superoxide-mediated  $\text{Fe(II)FZ}_3$  production rate, “background” signal associated with ferrozine enhanced reduction (before the addition of xanthine) was subtracted from the signal associated with superoxide mediated reduction (after the addition of xanthine). Superoxide was generated at a constant rate of  $90 \text{ pM s}^{-1}$  in seawater containing  $50 \text{ }\mu\text{M}$  xanthine and 1 unit  $\text{L}^{-1}$  xanthine oxidase.



**Figure S2.** Bimolecular dismutation of superoxide in seawater (pH 8.2). Irradiated 1 mM borate buffer was added to seawater containing 15 $\mu$ M DTPA to provide a final concentration of 10 nM superoxide. The superoxide concentration was then monitored by measuring superoxide-mediated MCLA chemiluminescence. The data are the average of triplicate experiments.



**Figure S3.** Calculated concentration of Fe(III)' in seawater with and without superoxide and ferrozine at the concentrations of (a) 50 nM Fe and (b) 500 nM Fe. The gray solid and dashed lines show the concentration of Fe(III)' without superoxide and ferrozine calculated using constant  $k_f$  and fitted  $k_f$ , respectively. The black solid and dashed lines show the concentration of Fe(III)' with superoxide and ferrozine calculated using constant  $k_f$  and fitted  $k_f$ , respectively. Rate constants ( $k_d^*$ ,  $k_f$  and  $k_{red}^*$ ) used in this calculation are shown in Table 2.