

Supplementary material: Calculation of Fe(II) Half Lives

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The calculation of Fe(II) half lives was done following the models of Santana-Casiano et
6 al. (2005, Model I) and Trapp and Millero (2007, Model II) at 4°C.

8 In Model I, the inorganic species taken into account are Fe^{2+} , $Fe(OH)^+$, $Fe(OH)_2$,
 $Fe(CO_3)$, $Fe(CO_3)_2$, and $Fe(CO_3)(OH^-)$.

10 In Model II, the inorganic species taken into account are Fe^{2+} , $Fe(OH)^+$, $Fe(OH)_2$, and
 $Fe(CO_3)_2$.

12 Input variables include ionic strength (I), pH, and dissolved inorganic carbon, all obtained
by CTD or shipboard measurements. CO_3^{2-} is calculated using data of alkalinity and total
14 dissolved inorganic carbon and the set of constants by Mehrbach et al (1973) after
Dickson and Millero (1987). H_2O_2 concentrations were measured on board (Bucciarelli et
16 al., in prep.). The water dissociation constant K_w is calculated as a function of
temperature (T) and ionic strength (I) (Millero et al., 1987). The OH^- concentration (free
18 scale) is then given by $K_w [H^+]^{-1}$.

20 The overall rate of oxidation of Fe(II) is given by:

$$\frac{d[Fe(II)]}{dt} = -[Fe(II)] \left([O_2] \sum_i \alpha_i k_{i,O_2} + [H_2O_2] \sum_i \alpha_i k_{i,H_2O_2} + [O_2^-] \sum_i \alpha_i k_{i,O_2^-} \right) \quad (2)$$

22 for Model I. The superoxide concentrations are assumed to equal $[O_2]/1000$ (Santana-
Casiano et al., 2005).

And by:

$$2 \quad \frac{d[Fe(II)]}{dt} = -[Fe(II)] \left([O_2] \sum_i \alpha_i k_{i,O_2} + [H_2O_2] \sum_i \alpha_i k_{i,H_2O_2} \right) \quad (3)$$

for Model II. Here the oxidation by the anion superoxide is assumed inside the oxygen
4 contribution.

k_{i,O_2} , k_{i,H_2O_2} , and k_{i,O_2^-} are the oxidation rate constants of the individual species for
6 oxidation by oxygen, hydrogen peroxide (the stoichiometry factor of 2 is already
considered in data from González-Dávila et al., 2005), and superoxide, respectively.

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The distribution coefficient of each inorganic Fe(II) species in seawater is given by :

$$10 \quad \alpha_i = \frac{K'_i [i]}{1 + \sum_i K'_i [i]} \quad (1)$$

where [i] is the inorganic ligand concentration and K'_i is the conditional stability constant
12 for each species.

14 Finally, the Fe(II) half life is given by:

$$t_{1/2} = \frac{\ln(2)}{(k'_{O_2} + k'_{H_2O_2} + k'_{O_2^-})} \quad (4)$$

16 where $k'_{O_2} = [O_2] \sum_i \alpha_i k_{i,O_2}$, $k'_{H_2O_2} = [H_2O_2] \sum_i \alpha_i k_{i,H_2O_2}$, and $k'_{O_2^-} = [O_2^-] \sum_i \alpha_i k_{i,O_2^-}$

for Model I, and by:

$$18 \quad t_{1/2} = \frac{\ln(2)}{(k'_{O_2} + k'_{H_2O_2})} \quad (5)$$

for Model II.

2 1. Calculation of K'_i

For both models, the conditional stability constants for each species (K'_i) are calculated as a function of T and I using the equations given by Trapp and Millero (2007, corrected via pers. com.):

$$\log_{10} K_i^* = \log_{10} K_i + A I + B I^{0.5} + C I^2 + \frac{D}{T} + E \ln(T) \quad (16)$$

with

	Fe(OH) ⁺	Fe(OH) ₂	Fe(CO ₃ ²⁻)	Fe(CO ₃) ₂
Log K _i	-218.186	-267.22	26.2876	6.7908
A	0.5	0.47	0.7	0.029
B	-1.1	-1.93	-2	-2.287
C	-0.02	-0.03	-0.031	-0.026
D	10120.8	12411.4	-2029.8	-88.68
E	33.1239	40.8906	-2.4676	0.1116

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For the species Fe(CO₃)OH, log K = 8.90 at 25°C and the same temperature coefficient as for Fe(CO₃)₂ is used (González-Dávila et al., 2005).

12 2. Calculation of k_{i,O_2}

For Model I, the following equations are used (rate constants in M⁻¹ s⁻¹).

$$\log k_{Fe^{2+},O_2} = 0.544 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right) \quad (5)$$

$$\log k_{FeOH,O_2} = 2.38 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right) \quad (6)$$

$$\log k_{Fe(OH)_2,O_2} = 6.06 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right) \quad (7)$$

$$\log k_{Fe(CO_3),O_2} = 0.6 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right) \quad (7)$$

$$\log k_{Fe(CO_3)_2,O_2} = 3.69 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right) \quad (8)$$

$$\log k_{Fe(CO_3)(OH) \cdot O_2} = 1.87 - 5861(1/T - 1/298.15) \quad (9)$$

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For Model II, the following equations are used (rate constants in $M^{-1} \text{ min}^{-1}$).

$$\ln k_{Fe^{2+} \cdot O_2} = 21 + 0.4I^{0.5} - 5562/T \quad (5)$$

$$\ln k_{FeOH \cdot O_2} = 17.1 + 1.5I^{0.5} - 2608/T \quad (6)$$

$$\ln k_{Fe(OH)_2 \cdot O_2} = -6.3 + 3.8I^{0.5} - 6211/T \quad (7)$$

$$\ln k_{Fe(CO_3)_2 \cdot O_2} = 31.4 + 5.6I^{0.5} - 6698/T \quad (8)$$

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3. Calculation of k_{i,H_2O_2}

10 For both models, the following equations are used (rate constants in $M^{-1} \text{ s}^{-1}$) from González-Dávila et al (2005).

$$\ln k_{Fe^{2+}, H_2O_2} = 38.0 - 9529/T \quad (17)$$

$$\ln k_{FeOH, H_2O_2} = 24.2 - 2757/T \quad (18)$$

$$\ln k_{Fe(OH)_2, H_2O_2} = 44.4 - 6658/T \quad (19)$$

$$\ln k_{Fe(CO_3), H_2O_2} = 33.2 - 6757/T \quad (20)$$

$$\ln k_{Fe(CO_3)_2, H_2O_2} = 65.6 - 14460/T \quad (20)$$

18 These equations explicitly correct for the effects of temperature on decay rates and because their experiments were done in seawater ($I=0.74$), no further corrections for relatively minor ionic strength differences were made. This treatment assumes that competition between O_2 and H_2O_2 is negligible (cf. González-Dávila et al., 2006), and

that pseudofirst-order decay constants are additive. We further assume that aside from the
2 effect of pressure on K_w , the effect of pressure on other equilibrium and rate constants is
negligible.

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4. Calculation of k_{i,O_2^-}

6 For Model I, the following equations are used (rate constants in $M^{-1} s^{-1}$).

$$\log k_{Fe^{2+}, O_2^-} = 3.84 - 282 \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (5)$$

8 $\log k_{FeOH, O_2^-} = 4.96 - 282 \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (6)$

$$\log k_{Fe(OH)_2, O_2^-} = 12.18 - 282 \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (7)$$

10 $\log k_{Fe(CO_3), O_2^-} = 2.94 - 282 \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (7)$

$$\log k_{Fe(CO_3)_2, O_2^-} = 9.6 - 282 \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (8)$$

12 $\log k_{Fe(CO_3)(OH), O_2^-} = 2.54 - 282 \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (9)$

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