Supplementary material: Calculation of Fe(II) Half Lifes


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

In Model I, the inorganic species taken into account are $\text{Fe}^{2+}$, $\text{Fe(OH)}^+$, $\text{Fe(OH)}_2$, $\text{Fe(CO}_3\text{)}$, $\text{Fe(CO}_3\text{)}_2$, and $\text{Fe(CO}_3\text{)}(\text{OH}^-)$.

In Model II, the inorganic species taken into account are $\text{Fe}^{2+}$, $\text{Fe(OH)}^+$, $\text{Fe(OH)}_2$, and $\text{Fe(CO}_3\text{)}_2$.

Input variables include ionic strength ($I$), pH, and dissolved inorganic carbon, all obtained by CTD or shipboard measurements. $\text{CO}_3^{2-}$ is calculated using data of alkalinity and total dissolved inorganic carbon and the set of constants by Mehrbach et al (1973) after Dickson and Millero (1987). $\text{H}_2\text{O}_2$ concentrations were measured on board (Bucciarelli et 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 scale) is then given by $K_w [\text{H}^+]^{-1}$.

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

$$\frac{d[\text{Fe(II)}]}{dt} = -[\text{Fe(II)}]\left[\sum_i \alpha_i k_{i,O_2} + [\text{H}_2\text{O}_2]\sum_i \alpha_i k_{i,H_2O_2} + [\text{O}_2^-]\sum_i \alpha_i k_{i,O_2^-}\right]$$

for Model I. The superoxide concentrations are assumed to equal $[\text{O}_2]/1000$ (Santana-Casiano et al., 2005).
And by:

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

(3)

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

\[k_{i,O_2}, \ k_{i,H_2O_2}, \text{ and } k_{i,O_2}^{-}\]

are the oxidation rate constants of the individual species for oxidation by oxygen, hydrogen peroxide (the stoichiometry factor of 2 is already considered in data from Gonzalez-Dávila et al., 2005), and superoxide, respectively.

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

\[
\alpha_i = \frac{K'_{i}[i]}{1 + \sum_i K'_{i}[i]}
\]

(1)

where \([i]\) is the inorganic ligand concentration and \(K'_{i}\) is the conditional stability constant for each species.

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

\[
t_{1/2} = \frac{\ln(2)}{k_{O_2}' + k_{H_2O_2}' + k_{O_2}^{-}'}
\]

(4)

where \(k_{O_2}' = \sum_i \alpha_i k_{i,O_2}\), \(k_{H_2O_2}' = \sum_i \alpha_i k_{i,H_2O_2}\), and \(k_{O_2}^{-}' = \sum_i \alpha_i k_{i,O_2}^{-}\) for Model I, and by:

\[
t_{1/2} = \frac{\ln(2)}{k_{O_2}' + k_{H_2O_2}'}
\]

(5)

for Model II.
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.):

$$\log_{10} K_i' = \log_{10} K_i + AI + BI^{0.5} + C I^2 + \frac{D}{T} + E \ln(T)$$  \hspace{0.5cm} (16)

with

<table>
<thead>
<tr>
<th>Species</th>
<th>$\log K_i$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$D$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)(^+)</td>
<td>-218.186</td>
<td>0.5</td>
<td>-1.1</td>
<td>-0.02</td>
<td>10120.8</td>
<td>33.1239</td>
</tr>
<tr>
<td>Fe(OH)(_2)</td>
<td>-267.22</td>
<td>0.47</td>
<td>-1.93</td>
<td>-0.03</td>
<td>12411.4</td>
<td>40.8906</td>
</tr>
<tr>
<td>Fe(CO(_3))(^-)</td>
<td>26.2876</td>
<td>0.7</td>
<td>-2</td>
<td>-0.031</td>
<td>-2029.8</td>
<td>-2.4676</td>
</tr>
<tr>
<td>Fe(CO(_3))(_2)</td>
<td>6.7908</td>
<td>0.029</td>
<td>-2.287</td>
<td>-0.026</td>
<td>-88.68</td>
<td>0.1116</td>
</tr>
</tbody>
</table>

For the species Fe(CO\(_3\))OH, $\log K = 8.90$ at 25ºC and the same temperature coefficient as for Fe(CO\(_3\))\(_2\) is used (González-Dávila et al., 2005).

2. Calculation of $k_{i,o_2}$

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

$$\log k_{Fe^{2+},o_2} = 0.544 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right)$$  \hspace{0.5cm} (5)

$$\log k_{FeOH,o_2} = 2.38 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right)$$  \hspace{0.5cm} (6)

$$\log k_{Fe(OH)_2,o_2} = 6.06 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right)$$  \hspace{0.5cm} (7)

$$\log k_{Fe(CO_3)^-,o_2} = 0.6 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right)$$  \hspace{0.5cm} (7)

$$\log k_{Fe(CO_3)_2,o_2} = 3.69 - 5861\left(\frac{1}{T} - \frac{1}{298.15}\right)$$  \hspace{0.5cm} (8)
For Model II, the following equations are used (rate constants in M\(^{-1}\) min\(^{-1}\)).

\[
\ln k_{Fe^{2+},O_2} = 21 + 0.4I^{0.5} - \frac{5562}{T}\tag{5}
\]

\[
\ln k_{FeOH\cdotO_2} = 17.1 + 1.5I^{0.5} - \frac{2608}{T}\tag{6}
\]

\[
\ln k_{Fe(OH)\cdotO_2} = -6.3 + 3.8I^{0.5} - \frac{6211}{T}\tag{7}
\]

\[
\ln k_{Fe(CO)\cdotO_2} = 31.4 + 5.6I^{0.5} - \frac{6698}{T}\tag{8}
\]

3. Calculation of \(k_{i,H_2O_2}\)

For both models, the following equations are used (rate constants in M\(^{-1}\) s\(^{-1}\)) from Gonzalez-Davila et al (2005).

\[
\ln k_{Fe^{2+},H_2O_2} = 38.0 - \frac{9529}{T}\tag{17}
\]

\[
\ln k_{FeOH,H_2O_2} = 24.2 - \frac{2757}{T}\tag{18}
\]

\[
\ln k_{Fe(OH)\cdotH_2O_2} = 44.4 - \frac{6658}{T}\tag{19}
\]

\[
\ln k_{Fe(CO)\cdotH_2O_2} = 33.2 - \frac{6757}{T}\tag{20}
\]

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. Gonzalez-Davila et al., 2006), and
that pseudofirst-order decay constants are additive. We further assume that aside from the 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 $k_{i, O_2}$

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

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

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

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

$$\log k_{Fe(CO)_2, O_2} = 2.94 - 282 \left( \frac{1}{T} - \frac{1}{298.15} \right)$$ (7)

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

$$\log k_{Fe(CO)_3, O_2} = 2.54 - 282 \left( \frac{1}{T} - \frac{1}{298.15} \right)$$ (9)
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