Steps towards a global model of photochemical cycling of iron

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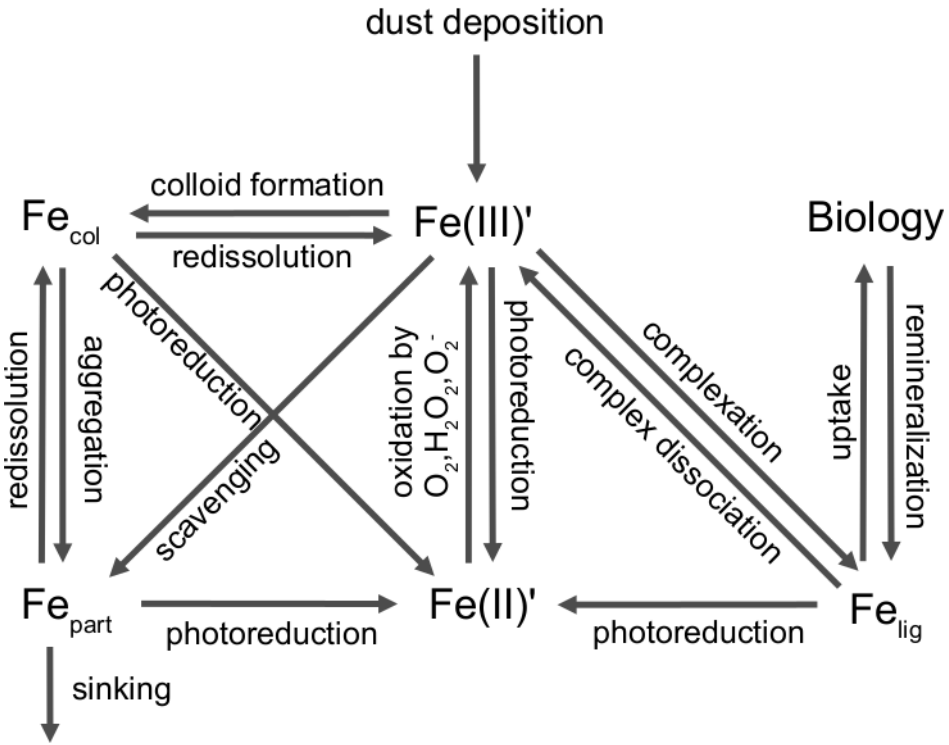
- .....

Redox reactions implemented first in 1D models: Weber et al. (2005, 2007) and Ye et al. (2009)

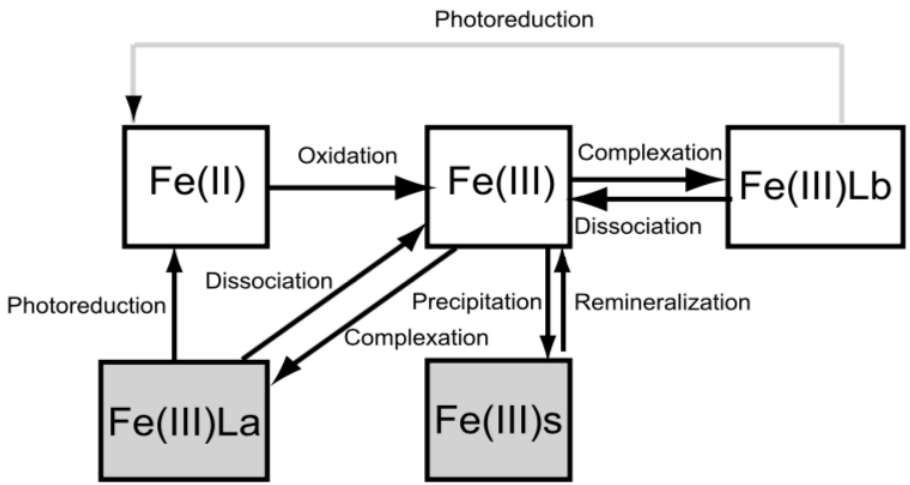


Ye. et al 2009

- photochemical production of O_2^-: proportional to irradiance;
- O_2 and H_2O_2 concentration fixed;
- no direct link to CDOM

Implementation in global models

- Tagliabue et al. (2009): first order impact of light and temperature on Fe speciation
- Tagliabeu and Völker (2011): numerical problem solved for different time steps of reactions in the iron cycle
  - fast reactions in equillibrium: redox and organic complexation
  - slow reactions: scavenging, uptake and remineralisation
- oxidation by O_2 considered but not that by H_2O_2 and O_2^-



Tagliabue et al. (2009)

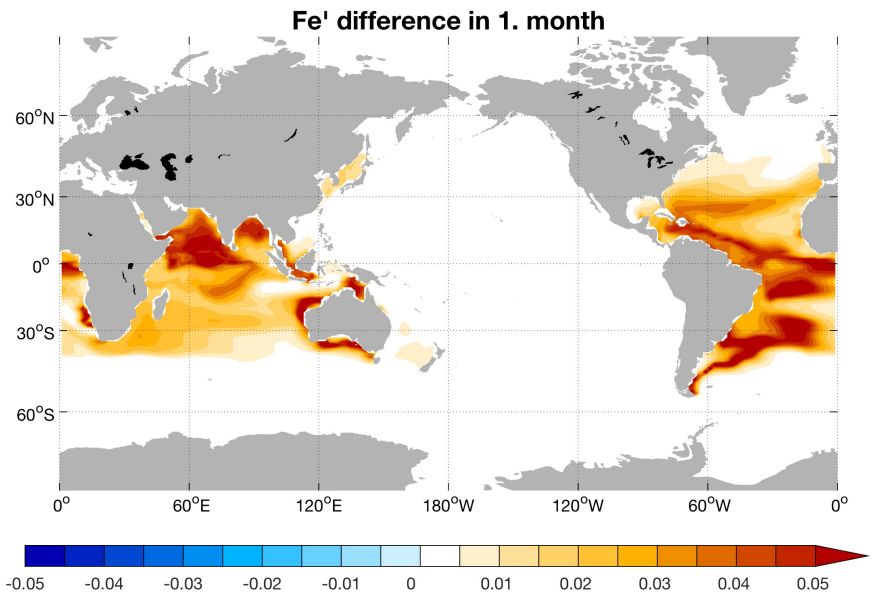
First step: offline calculation of redox species

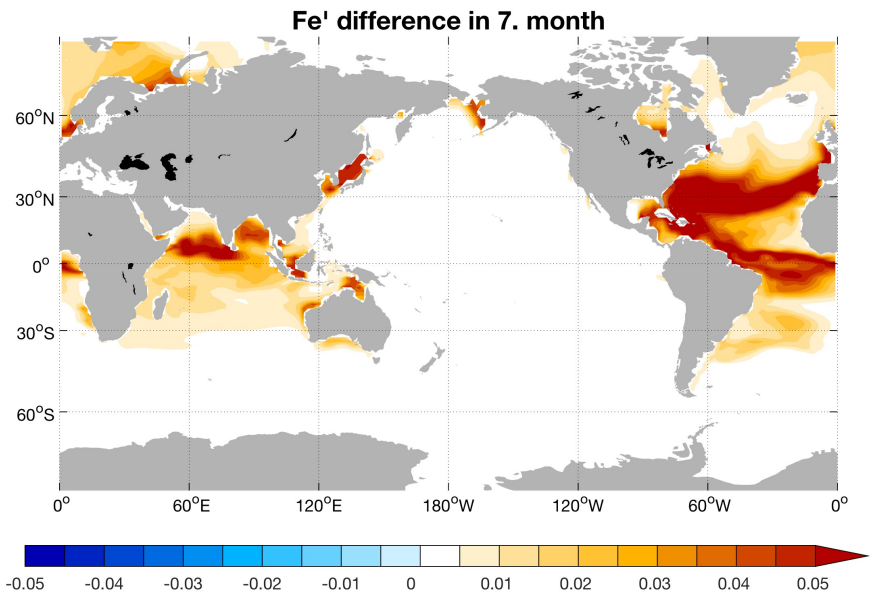
- redox species approach equilibrium;
- model output of DFe, total ligand and irradiance used as input;
- output species: Fe(III), Fe(II), FeL, L', O_2^-
- rate constants derived first from measurements at 25°C

$$\begin{aligned}\frac{\partial}{\partial t} Fe(II) &= k1_{red} \cdot Fe(III) + k2_{red} \cdot FeC + k3_{red} \cdot FeL \\ &\quad -(k_{ox}^{O_2} + k_{ox}^{H_2O_2} \cdot H_2O_2 + k_{ox}^{O_2^-} \cdot O_2^-) \cdot Fe(II)\end{aligned}$$

Effect of light on iron speciation: R_{ir0} and R_{const}

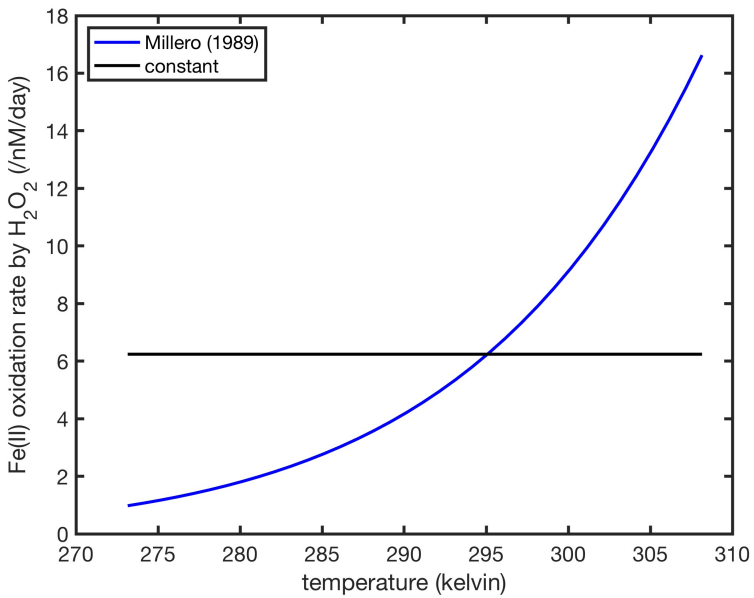
- two types of reactions depend on light: photoreduction of Fe(III), FeC and FeL, and production of O_2^-
- photochemical reactions result in higher concentration of free Fe in tropical and subtropical Atlantic and Indian Ocean

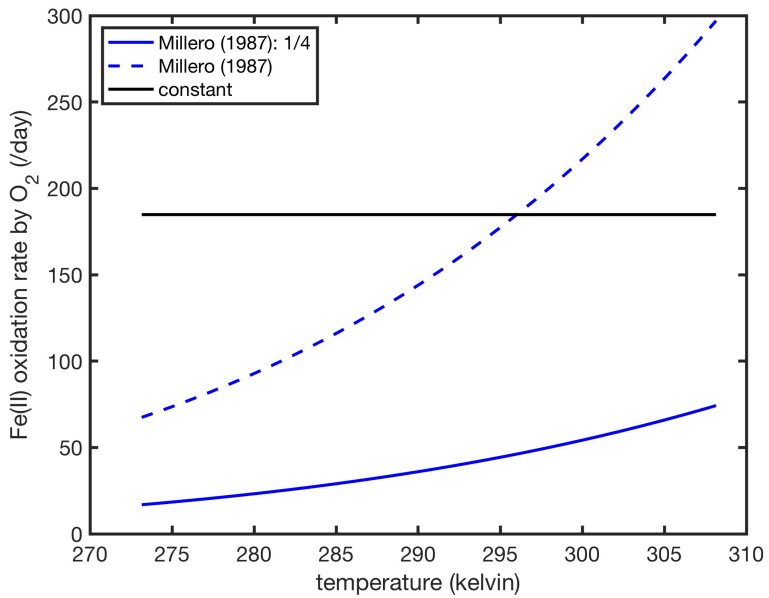




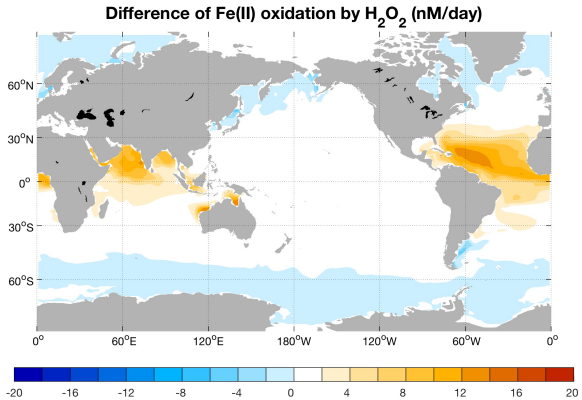
Temperature-dependent Fe(II) oxidation: R_{const} and R_{temp}

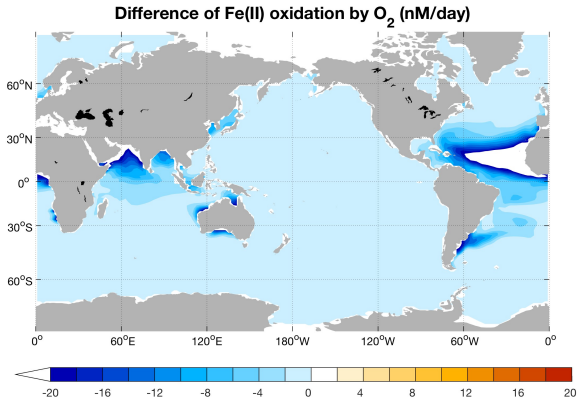
- functions fitted based on measurements at different temperatures (Millero and Sotolongo, 1989; Millero et al. 1987);
- $k_{ox}^{O_2}$ is assumed to be 1/4 of measured rates (Millero and Sotolongo, 1989; Moffet and Zika, 1987).

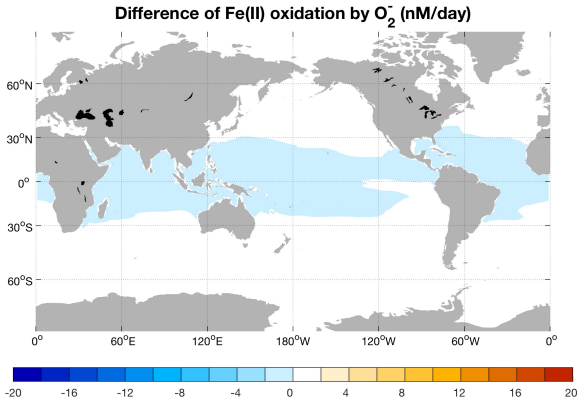




Effect on Fe(II) oxidation by H_2O_2, O_2 and O_2^-

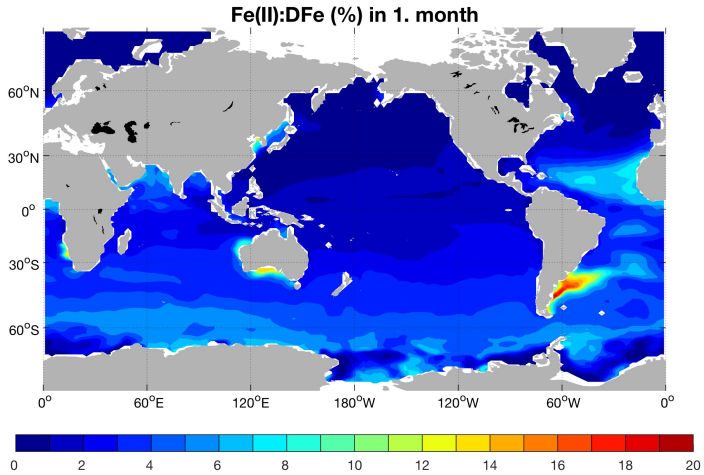


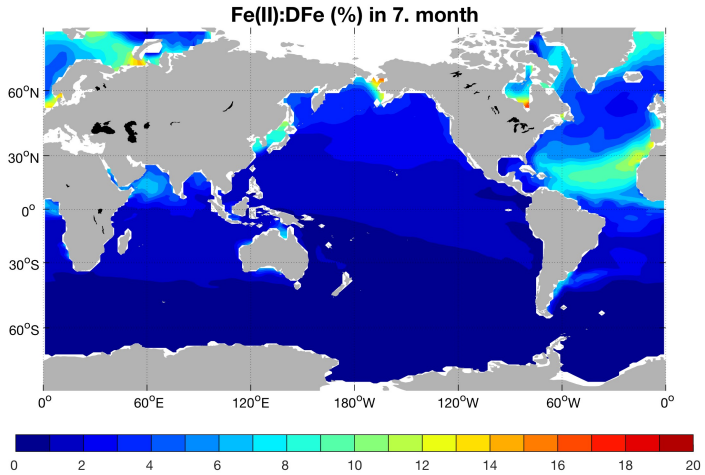


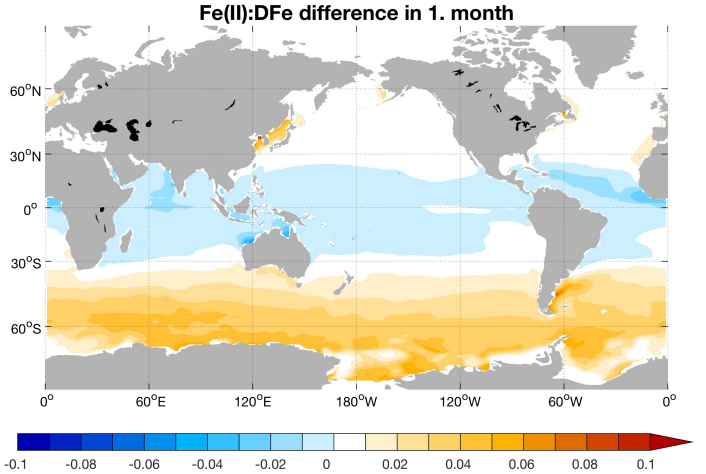


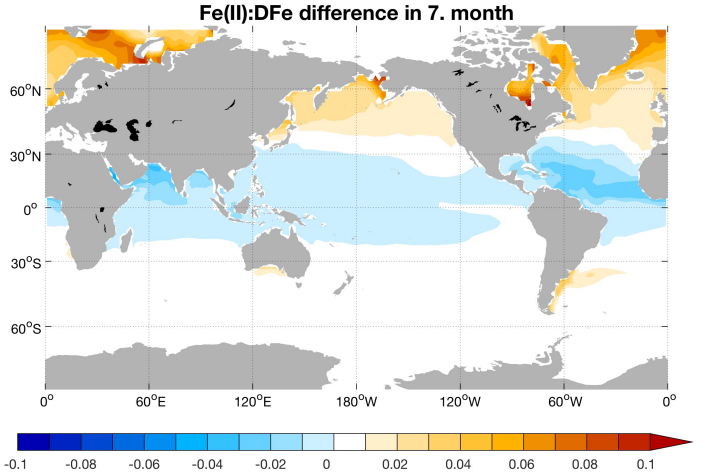
- oxidation by H_2O_2 dominates in the two runs R_{const} and R_{temp};
- oxidation by H_2O_2 increases at lower and decreases in higher latitudes
- oxidation by O_2 decreases, the stronger decrease at low latitudes is caused by the competition with H_2O_2 and lower O_2 saturation concentration;
- oxidation by O_2- decreases at lower latitudes and increases slightly in higher latitudes: oxidation by H_2O_2 and O_2 decreases in colder regions leading to more Fe(II) available for oxidation by O_2^-

Total effect on Fe(II) fraction









$\rightarrow$ strong increase in summer: high photoreduction of Fe(III) + lower oxidation

Effect of temporal and spatial variability of O_2^-: R_{cdom}

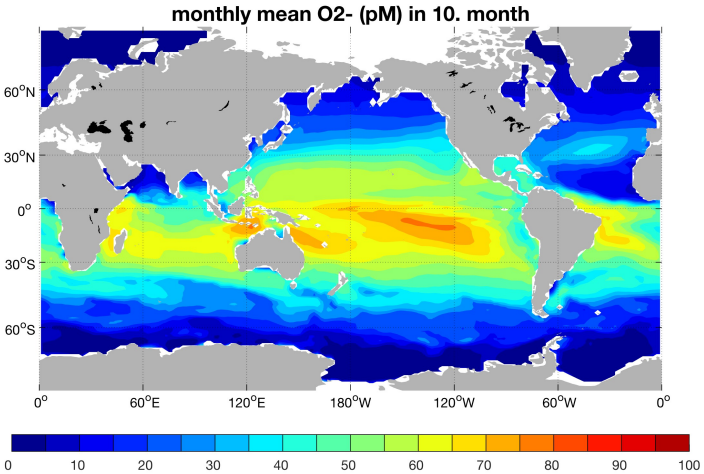
- R_{const}: related to irradiance;
- main process producing O_2^-: CDOM photochemical degradation
- equation of CDOM degradation according to Dutkiewicz et al. (2015)

$$\frac{\partial}{\partial t} O_2^- = r_{phot}^{CDOM} \cdot MIN(\frac{PAR}{k_{phot}}, 1.0) \cdot CDOM$$

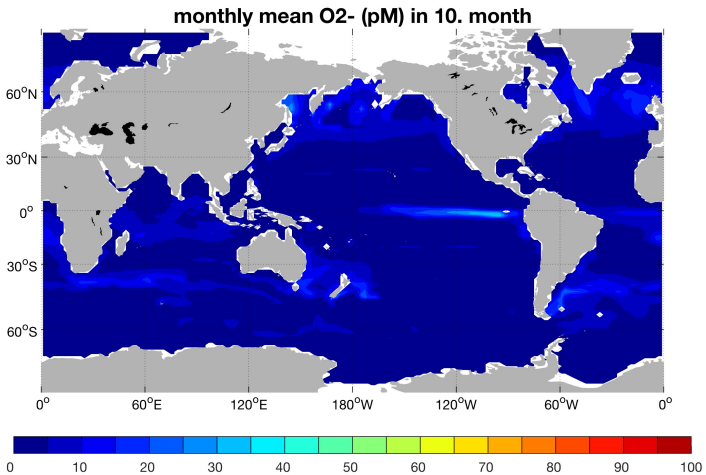
r_{phot}^{CDOM}: photochemical degradation rate of CDOM;
k_{phot}: light level for bleaching CDOM

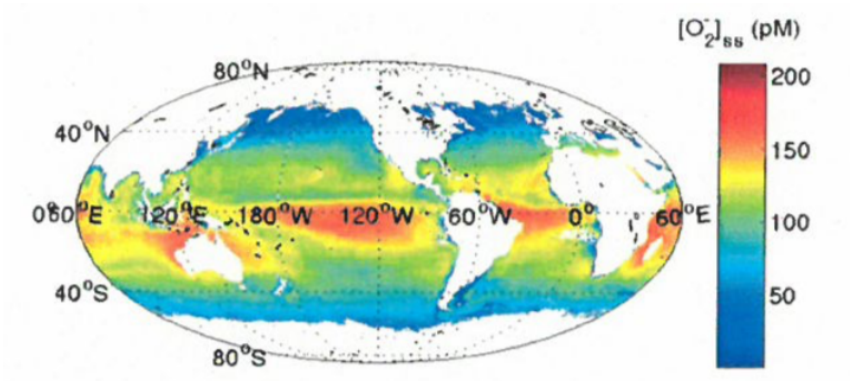
modelled spatial variability of O_2^-

R_{temp}



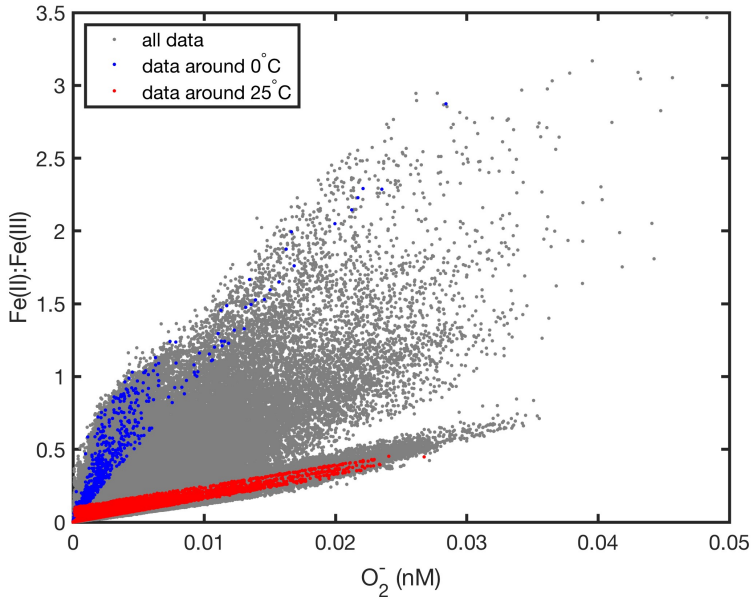
R_{cdom}





- Powers and Miller (2014): H_2O_2 production estimated from satellite data, dismutation and additional first-order sink of O_2^-;
- our calculation: constant H_2O_2 of 100 nM; O_2^- production estimated from CDOM photochemical degradation; dismutation and redox reaction with Fe and Cu as sink;
- midday steady state concentration compared with monthly averaged concentration!

Fe(II):Fe(III) ratio as a function of O_2^- concentration



- Fe(II):Fe(III) increases with O_2^-
- temperature controls the slope

Things that need to be discussed and/or tested in sensitivity runs

- role of H_2O_2 spatial variability
- role of Cu(I)/Cu(II) (so far constant total Cu of 1 nM used)
- O_2^- source from CDOM degradation
- uncertainties in assumptions of rate constants and their dependence on temperature and pH

After this: implementing into 3D global model! ☺