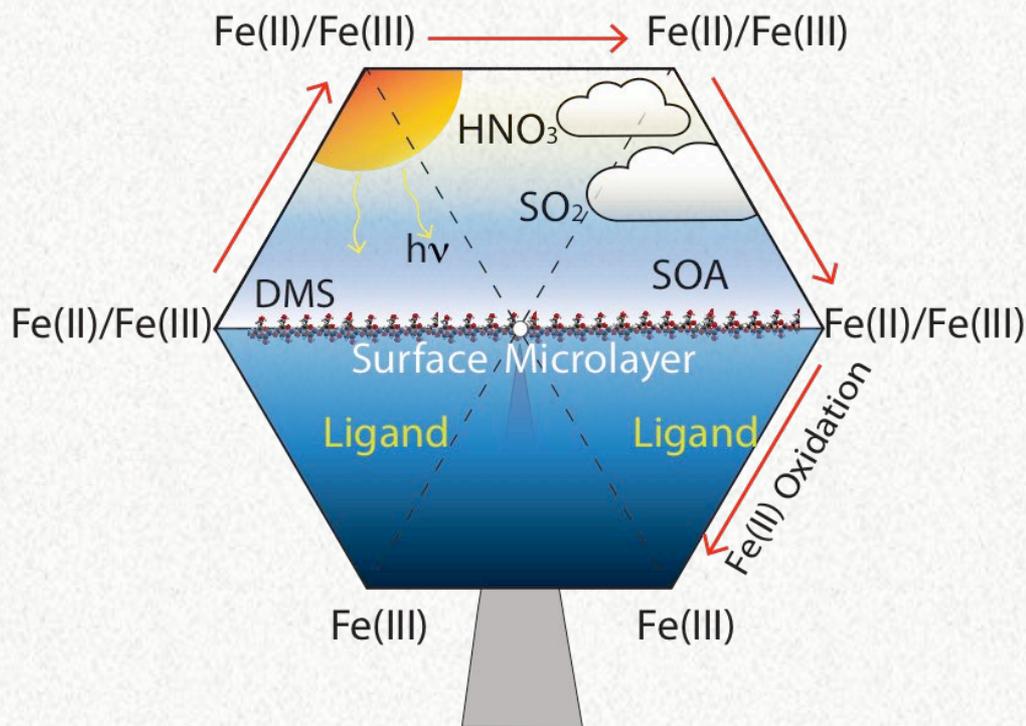


Effect of Atmospheric Organics on Aerosol Iron

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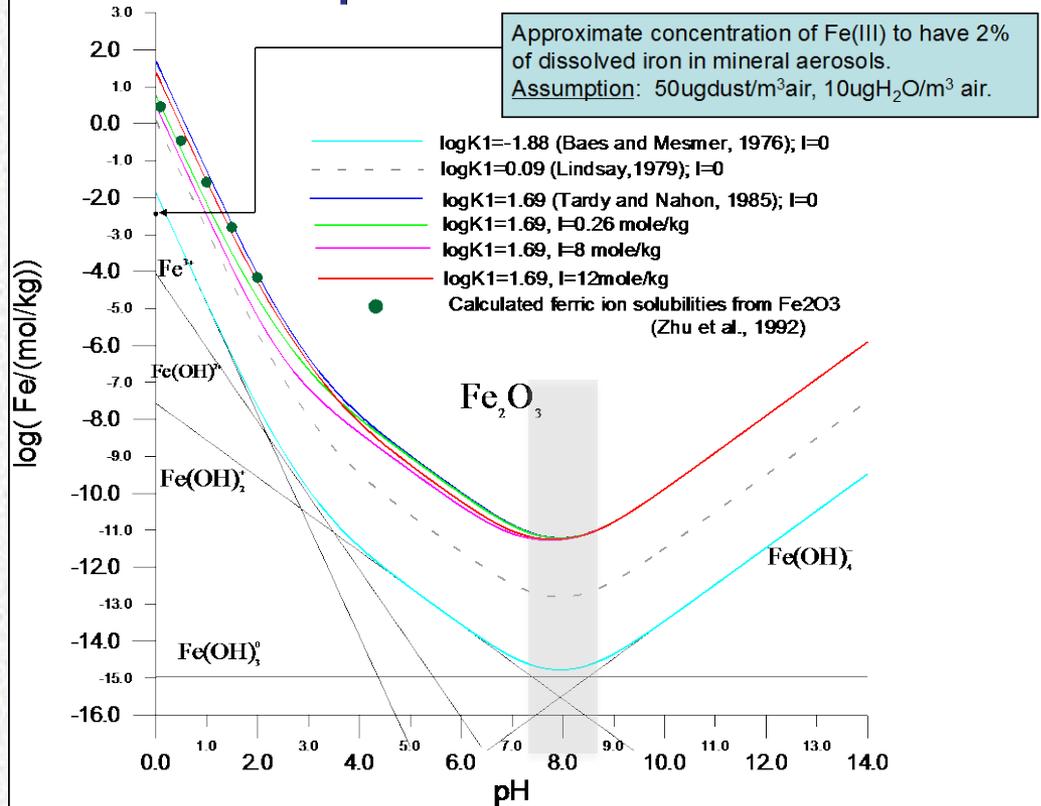
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Importance of Iron for life

- ✓ Iron (Fe) is so important that without it all life would cease to exist
- ✓ Every living thing: plants, animals, human beings, bacteria needs iron to survive and grow
- ✓ Plants require iron to make chlorophyll; animals, and human beings require iron to make DNA and hemoglobin
- ✓ The acquisition of Fe by aquatic life is hard, as the slow increase of oxygen during late Archaean and early Palaeoproterozoic times reduced the capacity of seawater to retain dissolved Fe

Iron in the Ocean

Concentrations of different hydrolysis species of Fe(III) in equilibrium with hematite



- Two orders of magnitude less than what is required to sustain current oceanic biomass
- **99%** of the bioavailable Fe in the world's oceans is bound to organic ligands
- Dust is currently regarded to be the principal source of external Fe for the open ocean
- In ocean literature bioavailable forms of Fe are operationally defined as a filtrate that passes through membrane with cut off value of ~ **0.4 μm**

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Table 8. Constants Used to Calculate Mineral Dissolution/Precipitation Rates Using Equation (22)

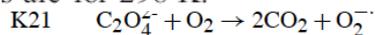
No.	Mineral	Kinetic Formations		Reaction Rates $M^{-n} s^{-1}$		Source
		Rate Constant K_r ($\text{mol}_{\text{mineral}} \text{ dissolved} / \text{m}^2 / \text{s}$)	m	A_i , $\text{m}^2 \text{ g}^{-1}$	$W_i \text{ g(Mineral) / g(Dust)}$	
RS1	calcite	$7.0 \times 10^{-2} \exp[1200(1/298-1/T)]$	1	0.1	11	<i>Morse and Arvidson</i> [2002]; <i>Alkattan et al.</i> [1998]; <i>Chou et al.</i> [1988]; <i>Sjöberg</i> [1976]
RS2	albite	$2.4 \times 10^{-10} \exp[7200(1/298-1/T)]$	0.5	1.0	17	<i>Blum and Stilling</i> [1995]; <i>Hodson</i> [1999]
RS3	microcline	$2.0 \times 10^{-10} \exp[6600(1/298-1/T)]$	0.5	1.0	8	<i>Blum and Stilling</i> [1995]; <i>Hodson</i> [1999]
RS4	illite	$1.3 \times 10^{-11} \exp[6700(1/298-1/T)]^{(1)}$	0.39	90	20	<i>Nagy</i> [1995]; <i>Tessier</i> [1990]; <i>Skopp</i> [2000]
RS5	smectite	$8.1 \times 10^{-12} \exp[6700(1/298-1/T)]^a$	0.3	300	8	<i>Nagy</i> [1995]; <i>Tessier</i> [1990]; <i>Skopp</i> [2000]
RS6	kaolinite	$4 \times 10^{-11} \exp[6700(1/298-1/T)]$	0.1	20	5	<i>Carroll and Walter</i> [1990]; <i>Nagy</i> [1995]; <i>Skopp</i> [2000]
RS7	hematite	stage I (0 to 0.8% of total oxide dissolved) $4.4 \times 10^{-12} \exp[9.2 \times 10^3(1/298-1/T)]$ stage II (0.8 to 40% of total oxide dissolved) $1.8 \times 10^{-11} \exp[9.2 \times 10^3(1/298-1/T)]$ stage III (40 to 100% of total oxide dissolved) $3.5 \times 10^{-12} \exp[9.2 \times 10^3(1/298-1/T)]$	0.5	100	5	<i>Azuma and Kametani</i> [1964]; <i>Blesa et al.</i> [1994]; <i>Cornell and Schwertmann</i> [1996]; <i>Zinder et al.</i> [1986]; <i>Skopp</i> [2000]

^aAverage activation energy for kaolinite [*Carroll and Walter*, 1990] is used.

Table 7. Equilibria Describing the Dissolution/Precipitation of Minerals Contained in Dust

No.	Equilibrium Reaction	Equilibrium Constants ^a	
		K_{eq} , mol^2/kg^2	Source
REQ1	calcite $\rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	4.959×10^{-9}	<i>Meng et al.</i> [1995]
REQ2	albite + $4\text{H}^+ + 4\text{H}_2\text{O} \rightleftharpoons \text{Na}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4^0$	1.6×10^3	<i>Lindsay</i> [1979]
REQ3	microcline + $4\text{H}^+ + 4\text{H}_2\text{O} \rightleftharpoons \text{K}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4^0$	1×10^1	<i>Lindsay</i> [1979]
REQ4	illite + $6\text{H}^+ + 4\text{H}_2\text{O} \rightleftharpoons 0.4\text{K}^+ + 0.25\text{Mg}^{2+} + 1.7\text{Al}^{3+} + 4\text{H}_4\text{SiO}_4^0$	2.24×10^{10}	<i>Lindsay</i> [1979]
REQ5	smectite + $4\text{H}^+ \rightleftharpoons 0.8\text{Na}^+ + 0.4\text{Mg}^{2+} + 0.8\text{Al}^{3+} + 4\text{H}_4\text{SiO}_4^0$	4.79×10^2	<i>Lindsay</i> [1979]
REQ6	kaolinite + $6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O}$	2.8×10^5	<i>Lindsay</i> [1979]
REQ7	hematite + $6\text{H}^+ \rightleftharpoons 2\text{Fe}^{3+} + 3\text{H}_2\text{O}$	4.4×10^{-1}	<i>Blesa et al.</i> [1994]

^aAll K_{eq} values are for 298 K.



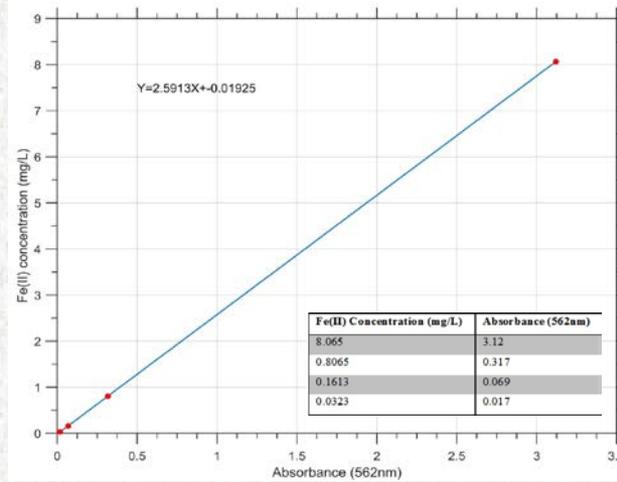
2.0×10^7

CAPRAM

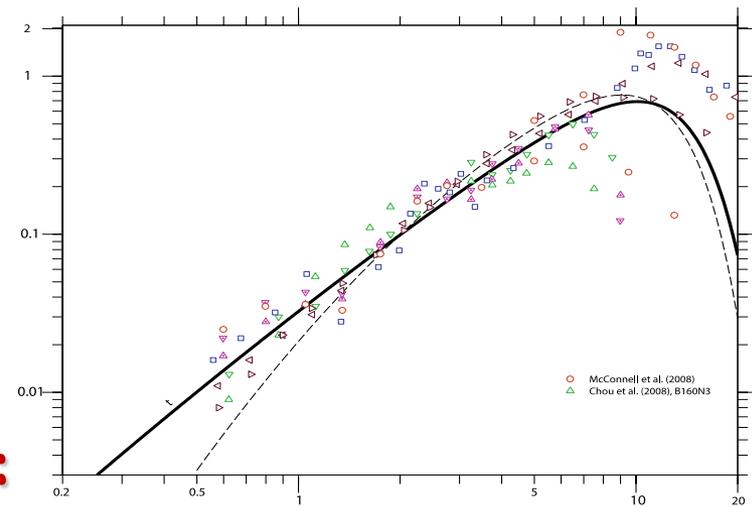
* $n = 1, 2$.

Laboratory studies:

Examine the potential of specific organic ligands to influence the lifetime of atmospherically delivered soluble Fe after its deposition to the ocean



Oxalic, malonic, citric, humic acid and a xanthan gum



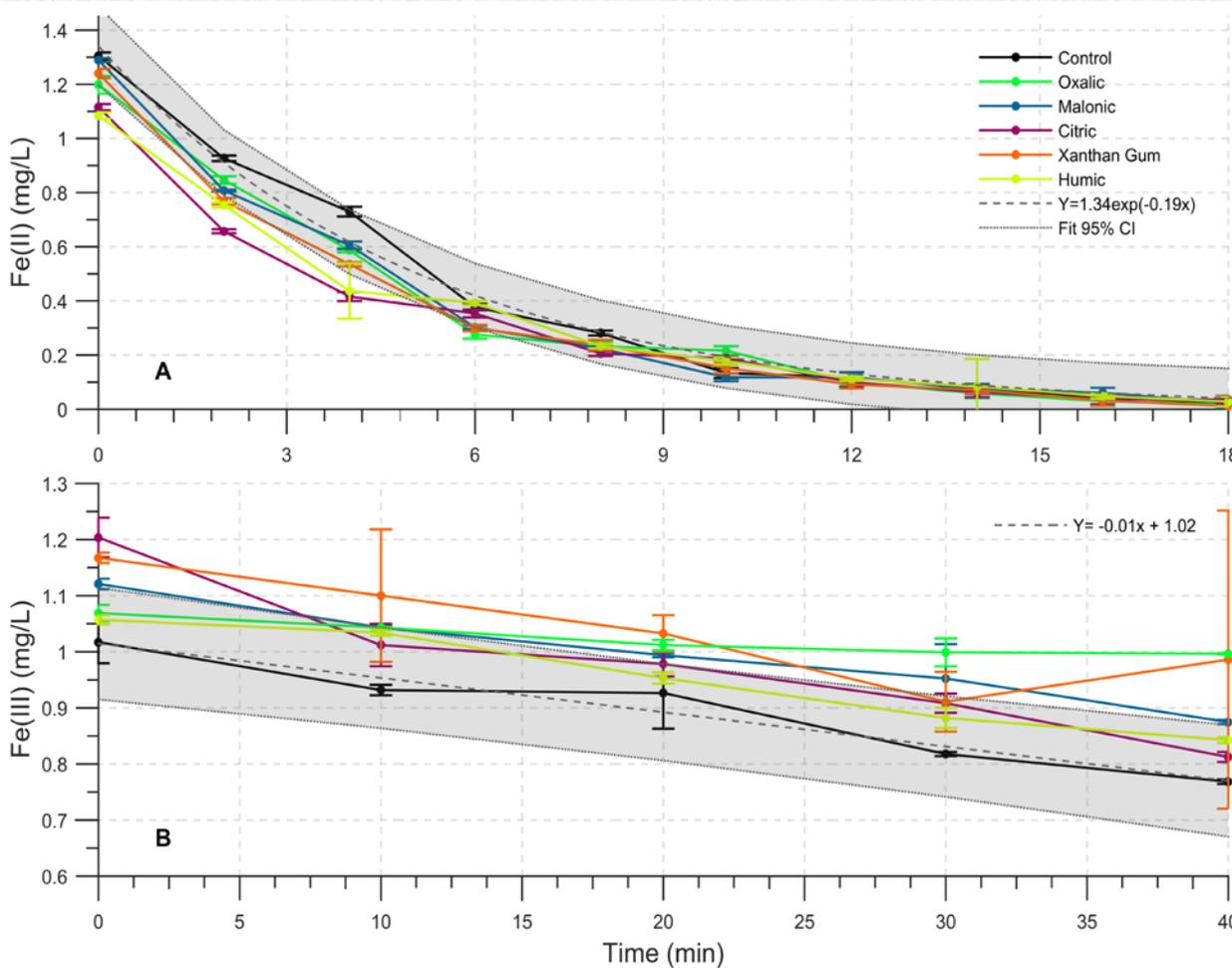
GEOS-Chem model simulations:

Adapted from Mahowald et al., 2014

Explore the possible overprediction of soluble Fe when it is assumed that dust particles with a diameter less than 0.4 μm contain 100% soluble Fe

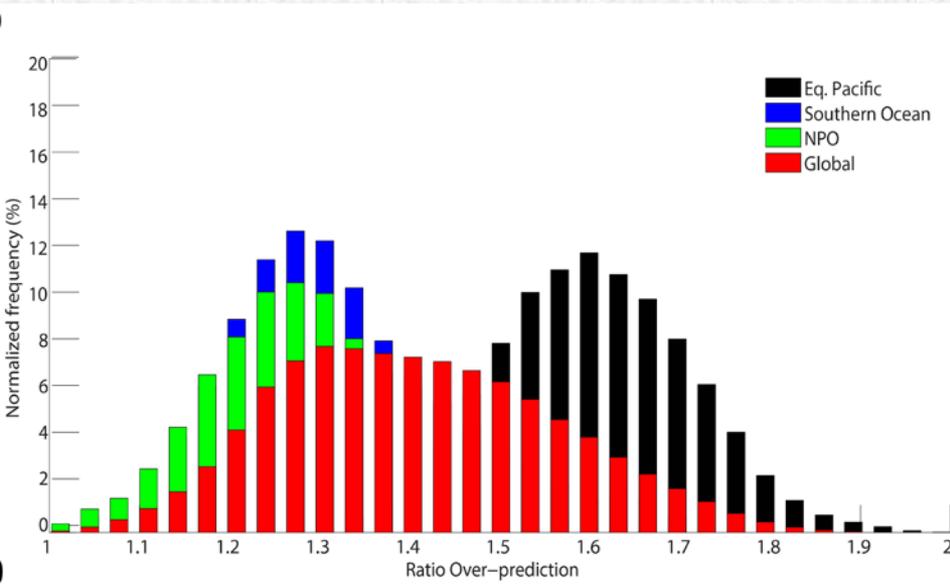
$$R = \frac{([Dust_{tot}] - [Dust_{0.4}]) \times Fe_w \times Fe_d + [Dust_{0.4}] \times Fe_w}{[Dust_{tot}] \times Fe_w \times Fe_d}$$

Ligand bonded Fe

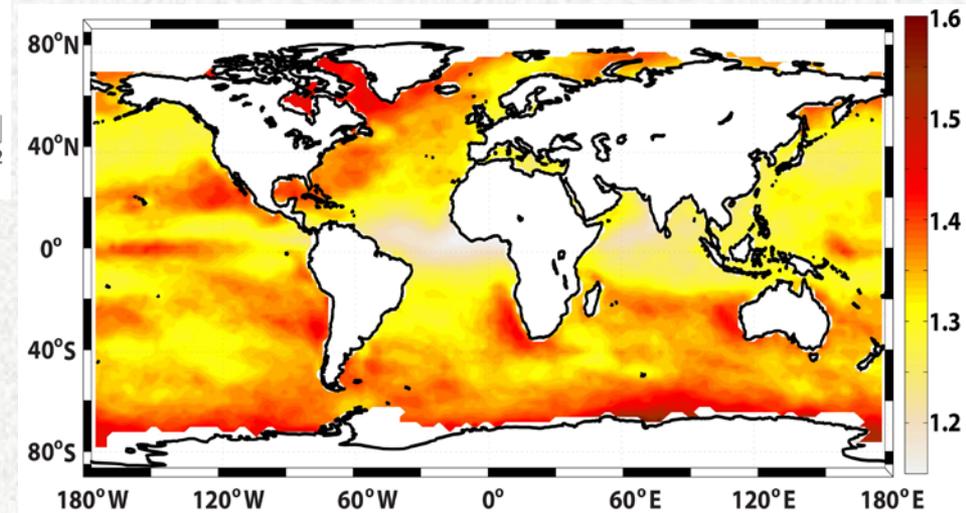


- In seawater the lifetime of soluble Fe(II), before oxidation to Fe(III), is less than 20 minutes
- None of the organic ligands had any influence of the lifetime of Fe(II)
- Hydroxylamine hydrochloride reduces amorphous Fe oxyhydroxides and therefore is not an adequate method to study soluble Fe

Overprediction of soluble Fe



- Applying the same operational definition of soluble Fe developed for the Fe in the ocean to atmospheric aerosols may lead to erroneous conclusions



- Tested organic compounds of atmospheric origin did not possess Fe(II) chelating properties
- Assumption that Fe in aerosol that pass through 0.4 μm diameter filter is fully bioavailable may lead over 60% overestimation of bioavailable Fe fluxes to the oceans
- Clarification is needed on oceanic lifetime and bioavailability of amorphous phases of Fe(III)
- New chemical measurements need to explicitly segregate different forms of Fe(III) (amorphous, aqueous, and ligand bound ones) in atmospheric aerosols
- Future studies should develop improved measurement techniques capable to chemically measure the speciation of Fe (in different size fractions) that are truly bioavailable in seawater